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Studies of Electrochemical Polarization in Liquids of Several Ranges of Conductivity.

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Studies of Electrochemical Polarization in Liquids of Several Ranges of Conductivity

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MANUSCRIPT THESES

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Measurements were made of polarization effects in electrical conduction through dielectric liquids, saline solutions, and liquids in the conductivity range intermediate between the dielectric liquids and the solutions. Particular attention was given to liquids in the intermediate range since these measurements were the first made to correlate experimental data with the Jaffé, "Theory of Conductivity of Polarizable Media".

The liquids chosen for study were hexane with a conductivity of the order of 10^{-18} to 10^{-19} $(\text{ohm cm})^{-1}$, isopropyl ether with a conductivity of the order of 10^{-14} $(\text{ohm cm})^{-1}$, bromobenzene with a conductivity of the order of 10^{-10} $(\text{ohm cm})^{-1}$, and KCl solutions of conductivity of the order of from 10^{-2} to 10^{-6} $(\text{ohm cm})^{-1}$.

Three systems were used to make the measurements: A Lindemann electrometer for the hexane and isopropyl ether, the dc amplifier of a Knorr Albers microphotometer for isopropyl ether and bromobenzene, and a Jones bridge for the ac effects in water and KCl solutions.

The ac measurements were of resistance and capacitance of the solutions as a function of frequency, concentration, electrode separation, and electrode material. The dc measurements were of the time dependence of current through the liquid following discontinuities in the voltage applied to them.

The general agreement between the experimental results and the Jaffé theory is good in the cases of hexane, saline solutions, and isopropyl ether. In bromobenzene the polarization effects were masked by other electrochemical effects so that no definite conclusions can be drawn.

CHAPTER I

INTRODUCTION

The phenomenon of polarization in electrical conduction is very general and is significant whenever charge transport is associated with transport of matter of ionic dimensions. Polarization effects appear in the passage of electricity through gases, liquids and most solids. As a matter of fact, the only case in which polarization does not appear is in electronic band conduction in metals.

Considerable experimental work has been done in the field of polarization. Most of these efforts have been directed toward eliminating or avoiding it in order to obtain precise measurements on conductivity. In these experiments the opposite course has been followed, in that attention has been given to emphasizing rather than minimizing the polarization effects.

In an effort to avoid polarization in the measurement of electrolytic conductance, early investigators turned to the use of alternating current. F. Kohlrausch [1], the pioneer in this field, showed how the influence of polarization could be avoided by the use of large surface electrodes, high frequency, and large electrode separation.

Later the concept of "polarization capacitance" was introduced by Kohlrausch [2] when he showed that his observations could be correlated by the assumption that the electrolyte

acts like a resistance and capacitance in series. He made the first actual measurement of a polarization capacitance, for platinum, finding it to be very high.

The Kohlrausch model served numerous investigators for more than twenty years. It was improved by Wien [3] with the addition of what he called "excess resistance". In ac measurements at low frequencies (as low as 64 cps) Wien showed that the observed resistance was always higher than the actual bulk resistance of the electrolytic solution. Although Wien offered no theory of the concepts of "polarization capacitance" and "excess resistance", he made a thorough experimental study of their dependence on frequency, voltage, and the nature of the electrodes. His observations form a fairly complete survey except that he made no study of the influence of concentration.

The first attempt at the presentation of a theory was made by Warburg [4]. This theory is based on the differential equation of diffusion, and diffusion alone is assumed responsible for the polarization emf. A notable improvement was made by Krüger [5] who added the Helmholtz layer concept to Warburg's diffusion theory and thereby established the theory of polarization which was widely used for the next generation.

Along separate lines of investigation systematic measurements were being made on the conductance of liquid dielectrics, beginning as early as 1854. A bibliography containing the papers of the first half century in this field has been prepared

by Schweidler [6]. Of especial note in these papers is the wide variance of the specific conductivities reported for such liquids as benzene, carbon disulphide, petroleum ether, and hexane.

Special impetus was given to the study of dielectric conductance in 1902 when Pierre Curie discovered the effects which x-rays and radium produced on the electrical properties of such liquids. Notable among the many investigations along this line were those of Jaffé [8-14]. He was able to prepare samples of liquid, particularly hexane, which were sufficiently free of conduction impurities to give much lower values of conductivity than had been previously reported. Moreover, his conductivity values could be reproduced in different samples of a given liquid.

Jaffe's observations on these pure samples showed that hexane behaved much like a dense gas in that the saturation current was independent of the applied voltage and the temperature. By surrounding the sample with lead shielding he was able to reduce the current by 70% showing that this amount of the conductivity was caused by external radioactivity and cosmic rays. He also observed an asymmetry in the amount of current conducted for positive and negative applied voltages, and thus found it necessary to average the values of current in the two directions. He further observed a current decay following the application of voltage which was much more pronounced for the less pure samples and was almost entirely absent in his purest hexane.

In all of these investigations polarization effects were present. It was regarded mostly as an obstacle to be avoided or minimized rather than a subject upon which comprehensive research could be conducted. Consequently the contributions of conductance research were along the lines of dissociation, recombination, diffusion, and mobility rather than on polarization.

In the range of conductivity intermediate between that of dielectric liquids and electrolytic solutions very little research of value in polarization studies has been done. Even investigations of specific conductivity alone are not very numerous. One of the explanations is that most of these liquids are not suitable for conductance studies: some are difficult to prepare, many are unstable (particularly in the presence of electric fields), others are difficult to purify, a few are highly explosive, still others are chemically active with metal electrodes, and some even have all of these disadvantages. Here again the results vary widely as to the conductance values given by investigators. It was therefore deemed important to collect and to analyze data in this range.

Correlation of the polarization effects observed in all phases of electrical conduction came within the realm of possibility when in 1933 Jaffé published his "Theory of Conductivity of Polarizable Media". [15] It was originally applied to correlate the effects of polarization in crystals but it has been extended and applied to semiconductors [16, 17], electrolytic solutions [18-21], and dielectric liquids [20,22,23]. So far it has not been applied to the liquids having conductance

in the intermediate range. In all of the cases where it has been applied, it has been possible to fit the experimental data to the theory.

Polarization research began in the laboratories at this University in 1947 under the direction of Dr. Jaffé. Measurements of polarization in dielectric liquids were made by LeMay [22,23] and in electrolytic solutions by Schaeffer [24] and Weston [25]. However, in both the dielectric liquids and the electrolytic solutions several factors called for further investigation.

The purposes of the present investigation were to fill in some of the missing portions of the polarization studies, to repeat and verify some previous observations, to fit the theory to experimental data in the intermediate conductance range, and to present methods applicable to polarization studies in all ranges of liquid conductance.

CHAPTER II

A.C. MEASUREMENTS

As pointed out in the introduction considerable research has been directed toward determination of accurate conductivity data. Much valuable information on polarization has been obtained in connection with these measurements. Efforts in the conductivity research have led to improvements in measurement techniques as well as the development of techniques for avoiding polarization. It is the improvements in measurement methods that were of most use here. Jones and his collaborators [26-34] surveyed the experimental field rather completely and among other things developed a bridge which is excellent for normal conductance measurement [35].

A. The Bridge Assembly

Basically, the system used in these measurements consists of a Jones [35] bridge. The Jones bridge is specifically designed for the measurement of electrolytic conductance. However, certain aspects of the present research were different from the usual conductance measurements. Ordinarily, all possible provisions are made to minimize the capacitance and resistance due to polarization. Here, just the opposite techniques have been employed. As a result, it was necessary to modify and supplement the Jones bridge in a number of ways:

1. The insertion of series capacitors in the standard arm of the bridge.

2. The employment of a conductance cell with a guard ring. (This will be discussed separately)
3. The addition of an auxiliary Wagner ground to balance large effects due to the guard ring.
4. The use of a detector consisting of a null-meter amplifier, a wave filter, and a cathode ray oscilloscope.

A schematic diagram of the apparatus is shown in figure 1. Discussion will be given of those features which differ from the equipment usually used.

Since the large polarization capacitance appears in series with the large bulk resistance the measurements were made with series values. In this research values of series capacitance as high as 35 microfarads were measured and values up to 250 microfarads had to be balanced in the guard ring system.

The capacitance range of the Jones bridge is much too small for balancing such large values. In addition, the capacitors are in parallel with the resistors. Consequently, these were removed and a set of standard capacitors was calibrated and inserted as C_s in figure 1. The primary standards of the set were 0.001 mfd to 0.111 mfd, General Radio, mica, decade boxes. Additional paper, pyranol, and plasticon capacitors were calibrated in terms of the primary standards and were used with them to measure the large values of C_s.

The original Wagner ground of the Jones bridge is shown in figure 1 as R_3, R_4, R_5 and C_1. For reasons that will be

FIGURE I

A.C. BRIDGE ASSEMBLY

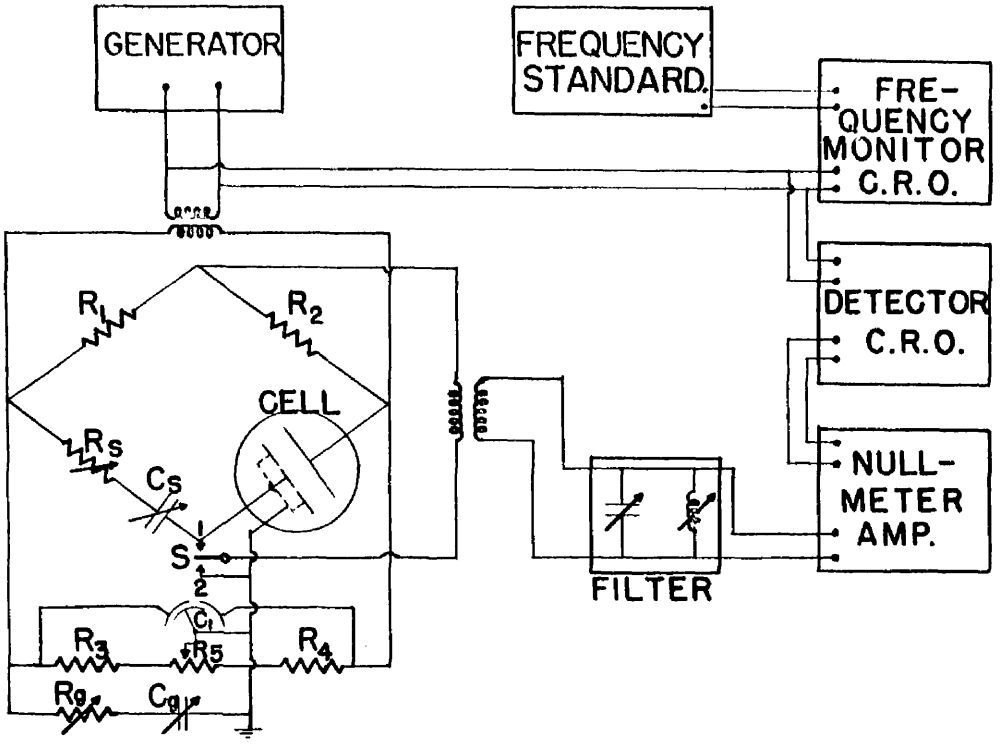
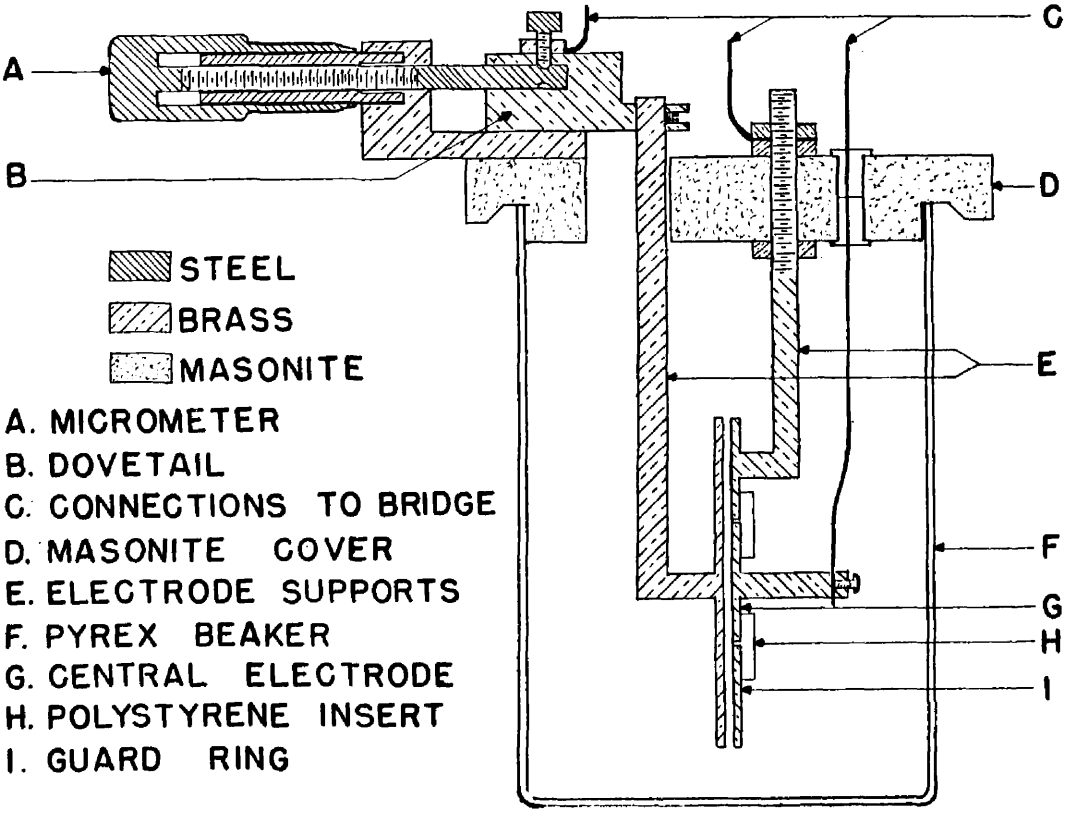


FIGURE II

A.C. CONDUCTANCE CELL



brought out, it was necessary to add an auxiliary Wagner ground consisting of R_g and C_g. R_g was a General Radio decade resistance box having a range of from zero to 11,111.0 ohms. C_g was a locally assembled arrangement of mica, pyranol and plasticon capacitors having a range of from zero to 250 mfd.

With a cell of conventional construction, balance can be achieved by successive adjustment of C_s and R_s with switch S in position 1, and then adjustment of R_5 and C_1 with S in position 2. This process is repeated until no disturbance is evident when S is switched back and forth between positions 1 and 2.

This procedure was somewhat modified in order to use the guard ring cell. For complete and proper balancing of the bridge with the present arrangment, stray effects due to the elements of the bridge and associated wiring were first balanced out by means of the bridge's original Wagner ground. This was done by balancing the bridge with C_g and R_g disconnected and a dummy impedance in place of the cell. From then on the bridge ground was left undisturbed and subsequent measurements with the actual conductance cell were made as previously described except that adjustments were made on R_g and C_g when the switch S was in position 2.

At balance, the central electrode and the guard ring were both at ground potential although there was no direct connection between them. The readings of C_s, R_s, C_g and R_g gave the values of the central electrode capacitance, the central electrode

resistance, the guard ring capacitance, and the guard ring resistance respectively.

The balance null was observed by means of a detector consisting of a General Radio amplifier Model 1231-B, and an Allen B. Dumont cathode ray oscilloscope Model 208-B connected as shown in figure 1. The wave filter was a locally assembled LC combination which could be adjusted to parallel resonance for any frequency from 100 cps to 30,000 cps. The output of the amplifier was connected to the vertical deflection amplifier of the detector-scope, while the generator was connected to the horizontal amplifier terminals of the detector-scope.

The amplifier was provided with a null-meter which was very convenient for obtaining an approximate balance. The final critical null was observed by causing the Lissajous ellipse on the screen of the detector-scope to degenerate into a horizontal line.

Two frequency standards were used. Sixty cps line voltage furnished a sufficient degree of accuracy at low frequencies and a calibrated electrically driven, 1000 cps tuning fork provided more accuracy than needed at medium and high audio frequencies. Frequency monitoring was done by simply maintaining the appropriate Lissajous figure on the monitoring oscilloscope screen.

With this arrangement precise measurements were made over a frequency range of from 18 cps to 18,000 cps, a resistance range of from 25 ohms to 50,000 ohms, and a capacitance range

of from .005 to 35 microfarads. The accuracy of observation was limited only by the accuracy of calibration of the standards and the stability of the conditions prevailing in the conductance cell itself.

B. The Conductance Cell for A.C.

The efforts of previous investigators to avoid the confusing influence of polarization are summed up by a quotation from Jones in which he confirms the earlier observations of Kohlrausch that ".....The error due to polarization is positive in sign and may be minimized and made practically insignificant by use of proper platinization, large electrodes, high frequency, and high resistance ....."[28,36]

Since the Jaffé theory is developed for the linear case, the cell had to be constructed so that the distribution of the field lines over the area in question would be as homogeneous as possible. Furthermore, since the polarization effects were to be maximized rather than eliminated, the electrode separation had to be small compared to the diameter of the measuring electrode. Finally, it was desirable to perform measurements at variable plate distances. These considerations led Schaeffer to construct and use a cell similar to the one shown in figure 2 [24]. The cell constructed by Schaeffer was improved by Weston and used for the accumulation of a considerable amount of data [25]. Weston's improvements consisted principally of elimination of strays within the cell due to conduction from the backs, edges, and supports of the electrodes.

In this research the cell was further improved and is shown in its final form in figure 2. From this drawing it will be seen that the electrode structure was that of a plane-parallel plate condensor with a guard ring. The central electrode was supported with its surface concentric and coplanar with the surface of the guard ring, by means of an annular polystyrene insert. The guard ring was supported by a rod bolted to the masonite top. The opposite electrode was supported by a rod rigidly fastened to a micrometer driven dovetail which provided for adjustment of electrode separation.

The edges, backs, and supports of the electrodes were covered with polystyrene coil dope to eliminate stray effects. The micrometer provided adjustment with an accuracy of 0.005 cm for the difference between successive settings. The masonite top was machined to fit the top of a Berzelius, tall form, 500 cc pyrex beaker from which the rim was removed. The electrolyte was placed in the beaker and the cell immersed in a constant temperature bath.

The important dimensions of the electrodes are as follows:

Radius of central electrode	1.017 cm
Inner radius of the guard ring	1.056 cm
Outer radius of the guard ring	3.018 cm
Effective area of the central electrode	3.36 cm^2

Measurements taken with this cell provided much important data, some of which will be presented here. However, it was apparent that variations took place within the electrolyte between the electrodes and at the surfaces of the electrodes.

These variations could neither be prevented nor controlled using a cell of this design. Later most of these variations were eliminated in a continuous flow cell used by Chang [21b].

C. Measurements

Before presenting the measurements and their results, it should be pointed out that they do not represent an attempt to obtain precision data of the kind realized by Jones and Christian [31], but rather to survey the field of investigation. Particular attention was directed toward:

(1) a wider range of frequency

(2) dependence on electrode separation of excess resistance and polarization capacitance

(3) the effect of different materials as electrode surfaces

Earlier observers have reported on the difficulty, or rather on the impossibility of obtaining reproducible results in the determination of the polarization capacitance and the excess resistance. Wien [3] in particular has pointed out the various difficulties and has expressed the opinion that they are mainly due to the changing conditions at the surfaces of the electrodes. This was confirmed by Jones and this circumstance would account for the fact that the values obtainable change, not only from one sample of the liquid to another, or from one set of electrodes to another, but that they also change with time for the same set of electrodes and the same sample of liquid. This "aging process" makes it quite impossible to determine absolute values, and special precautions

have to be taken, even to obtain relative values which are comparable.

Wien has confirmed his conclusions abundantly with detailed observational material. Observations from the research presented here, though based on much wider ranges of frequencies, are in complete agreement with his regarding the variability of the observed effects with uncontrollable circumstances. It follows also from theory that the source of the variability may be found in varying surface conditions. In the discussion of theory in Chapter IV, it will be seen that polarization capacitance and resistance depend strongly on a constant, ρ , which is determined by the charge transfer rate at the electrode boundary. Hence, variations of any nature at the electrode-electrolyte interface may be expected to cause large variations in the polarization effects.

No special efforts were made in this survey to obtain constant, or even reproduceable, surface conditions. Naturally, the procedures recommended by Wien were carefully observed. They consisted of keeping currents as low as possible and letting the electrodes and the solutions "age" sufficiently before taking final measurements. The latter point, however, involves a further inconvenience. Since the cell was not sealed from the atmosphere, the solution was bound to change its character.

The method of measurement finally adopted as most satisfactory will now be described briefly.

With the cell in place and the thermostat control set for regulation at the desired temperature, the equipment

was left undisturbed for several hours in order to let the surfaces approach equilibrium (to "age"), and to permit the temperature to stabilize. After this, the electronic circuits were turned on and allowed to warm up for about a half hour. A series of measurements was then commenced.

A single series of measurements consists of the determination of C_s, R_s, C_g, and R_g at each of a selected set of frequencies usually extending from 18 cps to 18,000 cps. Each determination was made by balancing the bridge as described previously. The measurements were made beginning with the lowest frequency and proceeding in ascending order of frequency until the highest was reached, whereupon the measurements were repeated in descending order of frequency. The corresponding ascending and descending values were averaged for each frequency, thereby eliminating the effects of variations that are linear with respect to time.

In the investigation of the dependence of capacitance and resistance on frequency and concentration, a series was made as described above on each of several concentrations and on a sample of the water used as a solvent. The water was prepared in a Barnstead Still, Model GL-$\frac{1}{2}$. All solutions for each group of series was made from a single distillate in order to assure the same solvent. The data thus obtained furnished sets such as the one presented in Table I.

For the investigation of the dependence of capacitance and resistance on frequency and distance, a series was made for each of several settings of the micrometer electrode adjustment.

These settings were made at intervals of .100 cm. The results of three such series are tabulated in Table II.

In order to study the effects of the electrode surface on capacitance and resistance, entire groups of series were duplicated with different surfaces on the electrodes. The electrodes, which were made of brass, were ground and polished to flatness before being electroplated. Studies with this cell have been made on polished nickel, gold, and platinized surfaces. Another cell with constant plate distance L = .172 cm was used to study aluminum surfaces. Sets of data such as that given in Table III were obtained.

The voltage dependence of capacitance and resistance was investigated only to determine the extent to which variations of applied voltage would affect the validity of measurements. With a given electrolyte, no significant shift of bridge balance could be observed when the applied voltage was varied from 0.015 volts rms to 0.150 volts rms. It was thus assured that there existed a suitable plateau and all measurements were made with an applied voltage of $0.10 \pm .02$ volts rms.

In discussing the accuracy of the measurements it is perhaps best to state the accuracy of the individual factors involved. By a careful examination of the prevailing circumstances the maximum errors are estimated as follows: frequency $\pm .1\%$, temperature $\pm 0.2^{\circ}C$ (which amounts to about 0.5% in resistance or capacitance): standard capacitors $\pm 1\%$, standard resistors $\pm .1\%$, and incremental plate distance $\pm 2\%$.

According to these estimates, the overall error should not

TABLE I

Observed values of series resistance and series capacitance of water and KCl of several concentrations and for various frequencies using gold electrodes.

m / f	Water		.0001 N		.0002 N		.001 N		.002 N	
	C_s	R_s	C_s	R_s	C_s	R_s	C_s	R_s	C_s	R_s
18	14.9	5554	16.8	1904	17.3	1216	20.0	412.0	---	---
33	13.2	5352	14.3	1833	15.0	1134	17.2	351.1	21.2	211.0
51	12.2	5268	12.9	1797	13.6	1106	15.6	325.1	19.2	189.2
75	10.6	5150	11.14	1774	12.1	1080	14.3	307.6	17.0	174.0
120	9.70	5031	10.15	1758	11.4	1061	12.9	294.2	15.2	161.9
180	8.53	4984	9.28	1745	10.2	1058	12.0	285.8	13.8	154.6
300	7.04	5144	8.13	1730	9.20	1045	10.9	279.2	13.0	148.4
420	5.36	5227	7.42	1722	8.54	1038	10.4	277.2	11.7	145.6
600	4.01	5250	6.65	1718	7.80	1030	9.77	274.7	10.3	142.4
1800	.94	5221	3.44	1714	5.14	1024	7.80	270.0	9.02	139.5
3000	.37	5180	2.02	1707	3.55	1029	6.65	268.6	7.87	139.0
9000	.049	5134	.355	1696	.865	1031	3.75	266.8	5.33	138.1
18000	.013	5086	.106	1690	.250	1031	1.76	266.8	2.75	137.7

Concentration, m, in gram equivalents/liter

Frequency, f, in cycles/second

Series capacitance, C_s, in microfirads

Series resistance, R_s, in ohms

Temperature ---- 26.8°C

Electrode separation --- 0.10 cm

TABLE II

Observed values of series resistance and series capacitance for water at various frequencies and for three values of electrode separation using gold electrodes.

L / f	L = 0.1 cm		L = 0.2 cm		L = 0.3 cm	
	C_s	R_s	C_s	R_s	C_s	R_s
18	16.0	5652	15.8	11,235	15.7	16,085
33	13.6	5656	13.4	11,215	12.8	15,950
51	12.0	5442	11.4	11,140	10.8	15,970
75	10.6	5433	9.80	11,105	9.00	15,940
120	8.88	5364	7.80	10,985	6.80	15,894
180	7.40	5410	6.00	11,048	4.90	15,879
300	5.51	5376	3.88	11,184	2.90	15,872
600	3.08	5316	1.73	11,094	1.12	15,819
1800	.722	5298	.319	10,749	.186	15,756
3000	.306	5280	.122	10,918	.075	15,603
9000	.043	5216	.018	10,575	.012	14,924
18000	.012	5049	.005	10,115	.004	14,090
30000	.004	5470	.002	9,210	.002	12,600

Electrode separation, L, in centimeters

Frequency, f, in cycles/second

Series capacitance, C_s, in microfarads

Series resistance, R_s, in ohms

Temperature ----- 26.8° C

TABLE III

Observed values of series capacitance, of .001 N KCl solution at various frequencies and for three electrode surfaces.

f	Gold Plated C_s	Aluminum C_s	Platinized C_s
18	20.0	5.86	-----
33	17.2	5.74	-----
51	15.6	5.48	-----
75	14.3	5.35	38.0
120	12.9	5.15	26.6
180	12.0	4.84	20.8
240	----	4.53	-----
300	10.9	4.33	13.8
420	10.4	4.18	7.80
600	9.77	3.85	4.91
1800	7.80	3.67	2.78
3000	6.65	3.38	1.71
9000	3.75	2.42	.584

Series capacitance, C_s, in microfarads

Frequency, f, in cycles/second

Temperature --- 26.8° C

exceed ± 2% for a fixed plate distance. Now, it was observed that discrepancies between corresponding values taken with increasing and decreasing frequencies were much larger than this. They amounted to about 4% in the R-values and up to 8% in the capacitances. Consequently, these large errors must be ascribed to changes in the surface condition of the electrodes, and to changes in the solvent. This last statement agrees with the observation that the errors were largest with "conductance water".

The accuracy at the upper end of the frequency range was limited by the bridge and associated wiring. It should be noted that the Jones bridge is not designed for high frequency use.

It was in the low frequency part of the range that accuracy was poorest. This was due in part to the difficulty of filtering 60 cycle pickup and harmonics in the bridge error signal. However, most of the difficulty seems to have been that changes in the surfaces caused larger variations in the frequency range where polarization effects are largest.

Summarizing, it is estimated that the relative measurements have an accuracy of ± 2% in the frequency interval between 300 cps and 5,000 cps, and are progressively less accurate as the ends of the range are approached.

D. Results of the Measurements

A large number of measurements were performed under varying conditions. The frequency usually varied from 18 cps to 18,000 cps, but a few measurements were taken down to 10 cps

and up to 30,000 cps. Besides conductance water solutions of KCl were investigated.

Since the theory assumes complete dissociation, the concentrations used were low; the molar concentrations, in g-equivalent per liter, extended from 10^{-4} to 10^{-2}.

The results are qualitatively so uniform that they may be summarized simply.

(1) Resistance. At low frequencies and for all distances of the electrodes, the resistance is higher than the normal value. This "excess resistance" falls off with frequency and disappears at frequencies between about 100 cps and 1000 cps, according to the resistivity of the liquid. The larger the resistance of the solution, the earlier the excess resistance ceases to be noticeable. At higher frequencies, over a wide interval, the resistance remains approximately constant at its normal value, and finally begins to drop below this normal value.

These features, except for the final drop, are shown in figure 3 which refers to four series of KCl of various concentrations and represents R_s as function of $f^{\frac{1}{2}}$. Here, and in all of the ac material $f^{\frac{1}{2}}$ (or its logarithm) has been used as absicissa because in the theory frequency appears in this form explicitly.

The final drop (not shown in figure 3) sets in earlier and is stronger, the higher the resistance of the liquid. It is therefore most noticeable for pure water and the solutions of lowest concentrations. This is brought out in figure 5, and also by the numbers of Table II.

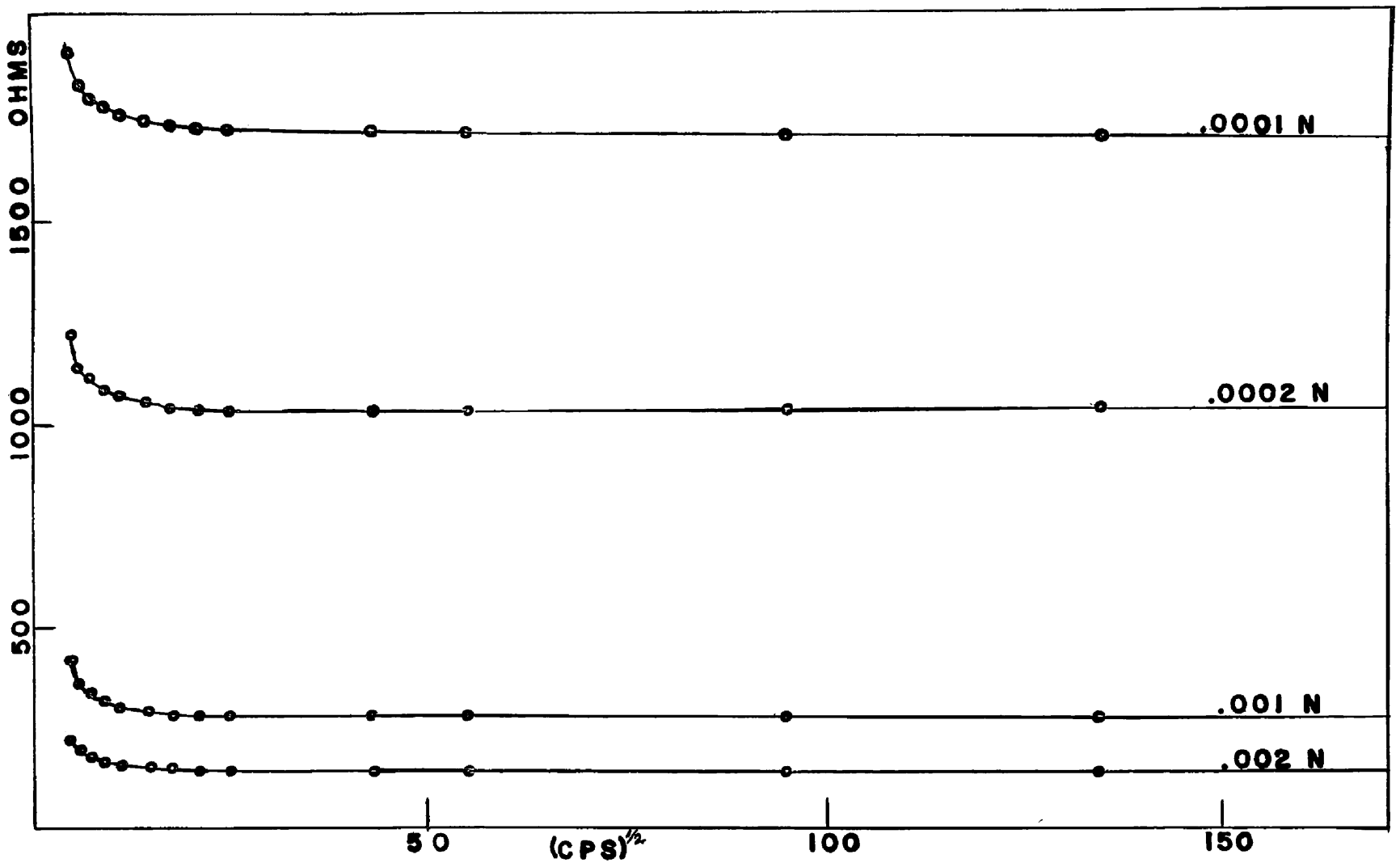


FIGURE III

RESISTANCE VS SQUARE ROOT OF FREQUENCY
FOR FOUR KCl SOLUTIONS

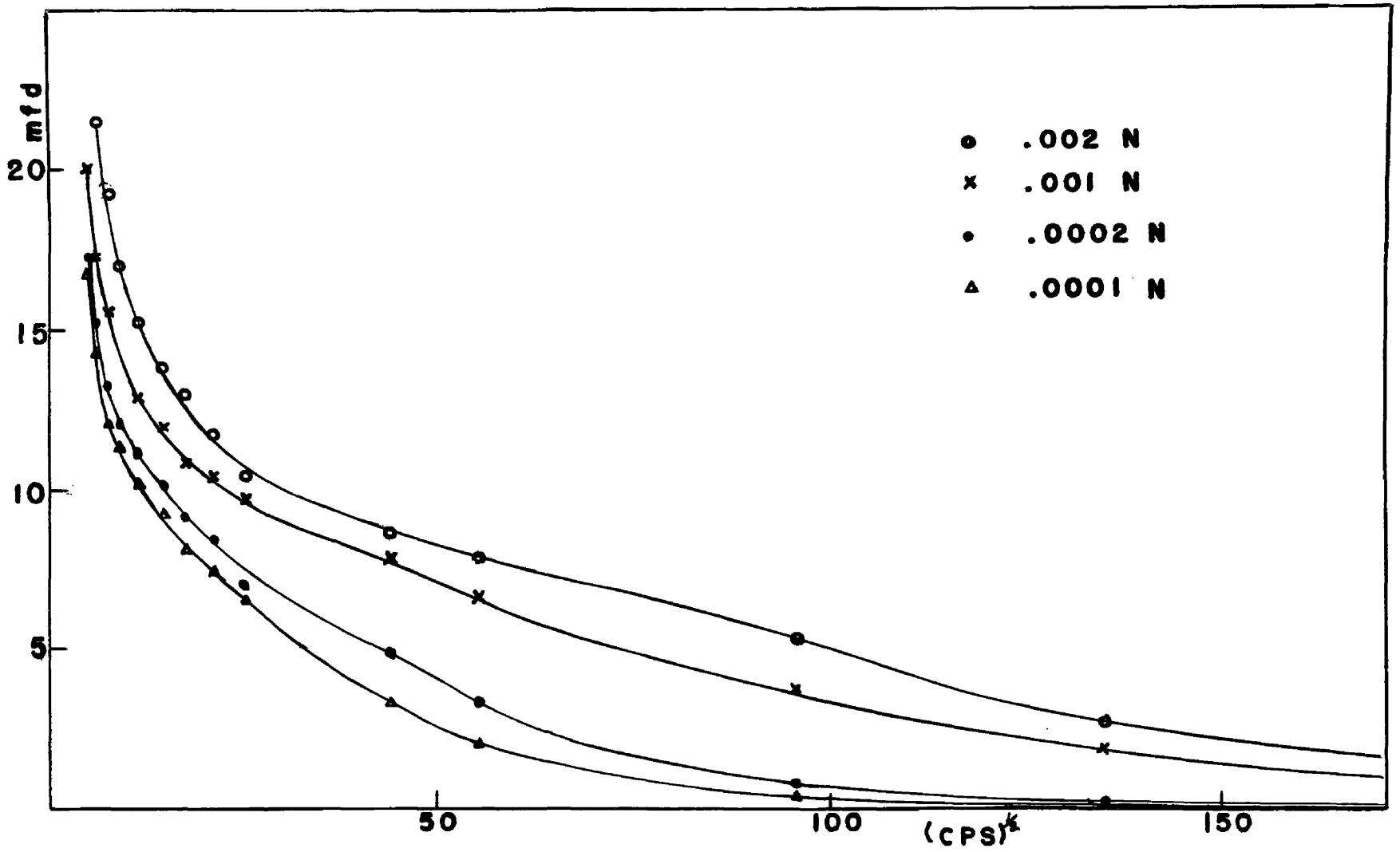


FIGURE IV
CAPACITANCE VS SQUARE ROOT OF FREQUENCY
FOR FOUR KCl SOLUTIONS

The excess resistance is independent of the electrode separation to a good approximation. This feature is brought out by figure 5 which is of R_s vs log $f^{\frac{1}{2}}$ for three values of electrode separation. For pure water the normal resistance is so high, of the order of 10^4 ohm, and the excess resistance so low, of the order 10^2 ohm, that the latter is often hidden by the uncertainties of the observations. The normal resistance, say observed between 1000 cps and 5000 cps, is a linear function of electrode distance.

The middle part of the resistance curves, which should represent the normal resistance freed of polarization effects, was never accurately constant, but invariably showed a slow decrease with increasing frequencies. This is a point of importance and will be discussed in Chapter V.

(2) Capacitance. For all series, the observed values of C_s decrease monotonically with increasing frequency over the entire range. It is, therefore, not feasible to distinguish the three portions of the curves as was done in the case of resistances. The high frequency end of the log C_s plot, however, is clearly marked by the rapid drop in C_s. According to the Jaffé theory, the low frequency end should approach a constant value, C_o, with decreasing frequency, but there is little indication of this in these measurements.

A_s for the dependence on electrode distance, all final measurements show that the observed capacitances are independent of the electrode separation for sufficiently low frequencies, in agreement with the observations of Jones and Christian [31].

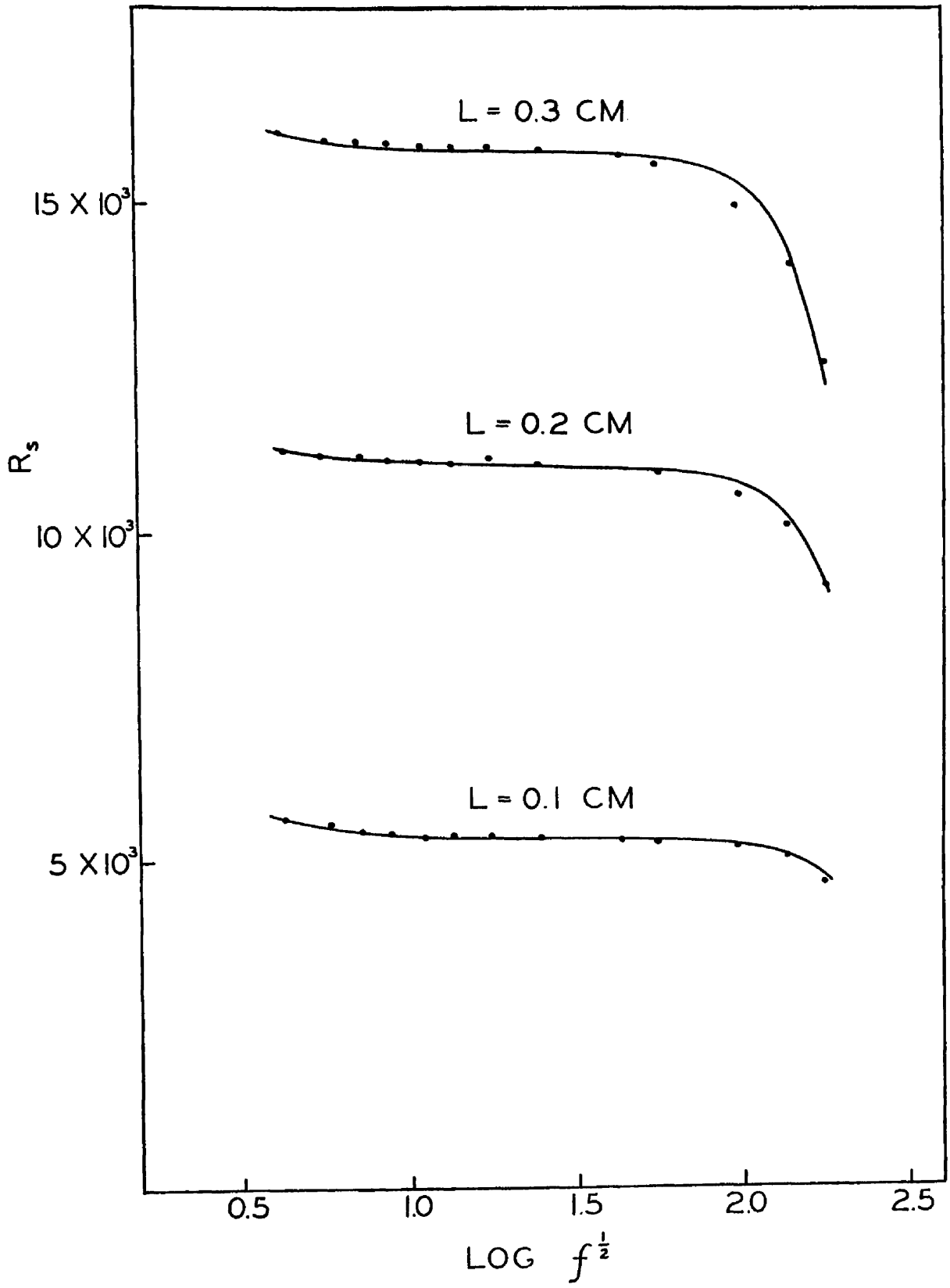


FIGURE V

RESISTANCE OF WATER VS Log $f^{\frac{1}{2}}$

FOR THREE VALUES OF ELECTRODE SEPARATION

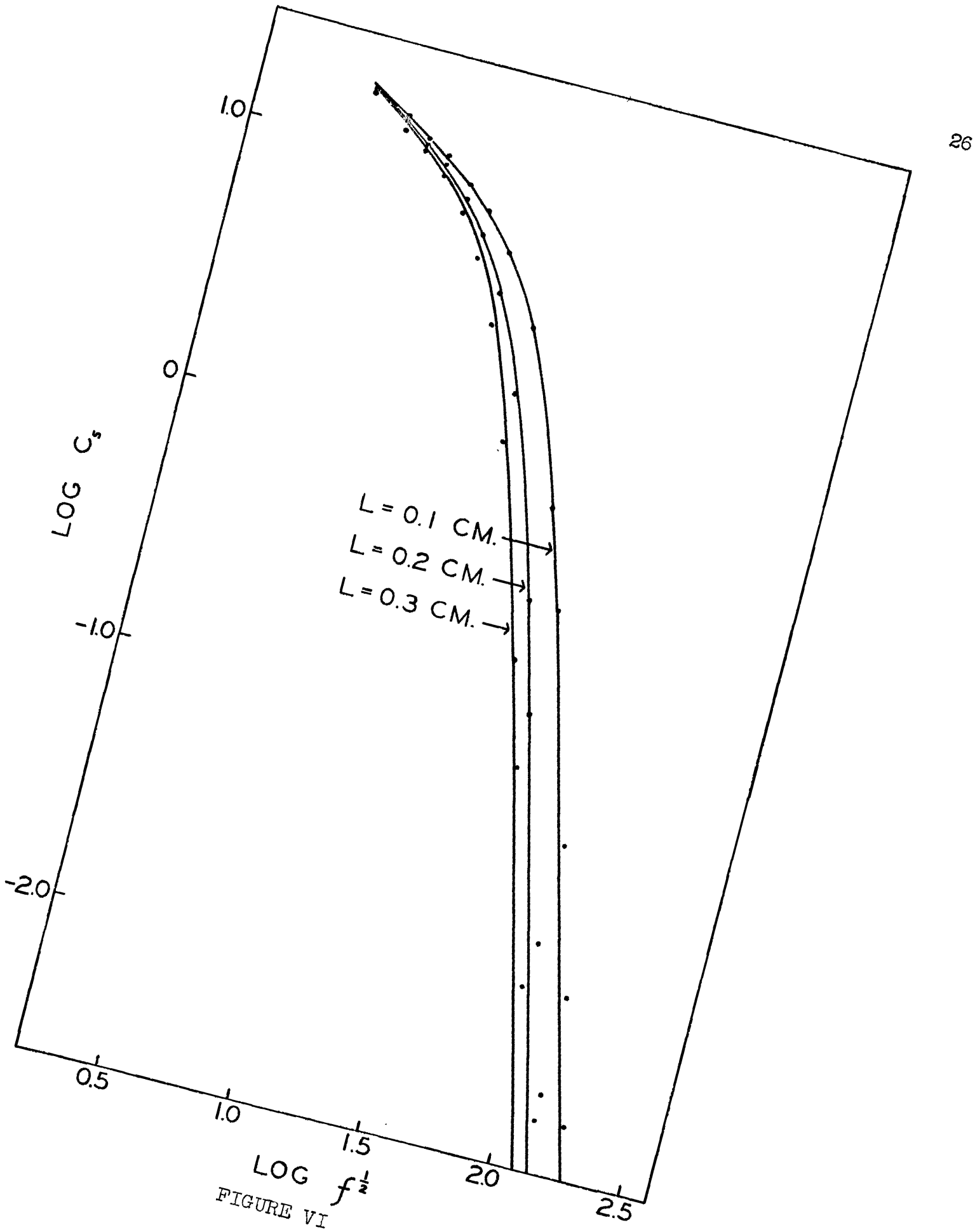


FIGURE VI

As the frequency rises the capacitance curves for different electrode separations separate, and arrange themselves in the order of the geometrical capacitances corresponding to each of the plate separations used. This separation occurs for lower values of the frequency and is more pronounced with liquids of higher resistance. These features are illustrated in figure 6 which shows log C_s plotted against 10 $(f)^{\frac{1}{2}}$ for water at three plate separations.

(3) Electrode material Complete sets of resistance and capacitance measurements were performed with Al, Ni, and Au electrodes. Since the character of the frequency dependence did not change with the electrode material for these metals (figure 7), it will be sufficient to show the influence of electrode material for the highest observed value of capacitance for each series, i.e. the capacitance at 18 cps. This has been done in Table IV which shows the equivalent values of parallel capacitance per unit area calculated from the observed values of C_s and R_s.

Some series of measurements were also performed on platinized surfaces, but it proved to be particularly difficult to obtain reliable results. The capacitances depended strongly on thickness and rate of deposition of the platinum and were extremely high at low frequencies, so high that they were beyond the capacitance range of the standards for frequencies below 75 cps. Another difficulty was that these surfaces showed a very marked "aging" effect, the capacitances decreasing with time. The foregoing features of platinized surfaces have

TABLE IV

Parallel equivalent capacitances, at 18 cps, for water and KCl solutions with different electrode surfaces.

Electrode surface	H_2O	KCl solutions of different concentrations, m					
		10^{-4}	5×10^{-4}	10^{-3}	2×10^{-3}	5×10^{-3}	10^{-2}
Al	1.21	1.56	1.58	1.72	----	1.90	1.84
Ni	2.36	2.89	3.87	3.68	4.05	4.17	4.29
Au	1.78	4.17	4.52	5.50	----	----	7.16

Concentration, m, in gm-equivalent/liter

$25^{\circ}C < T < 27^{\circ}C$

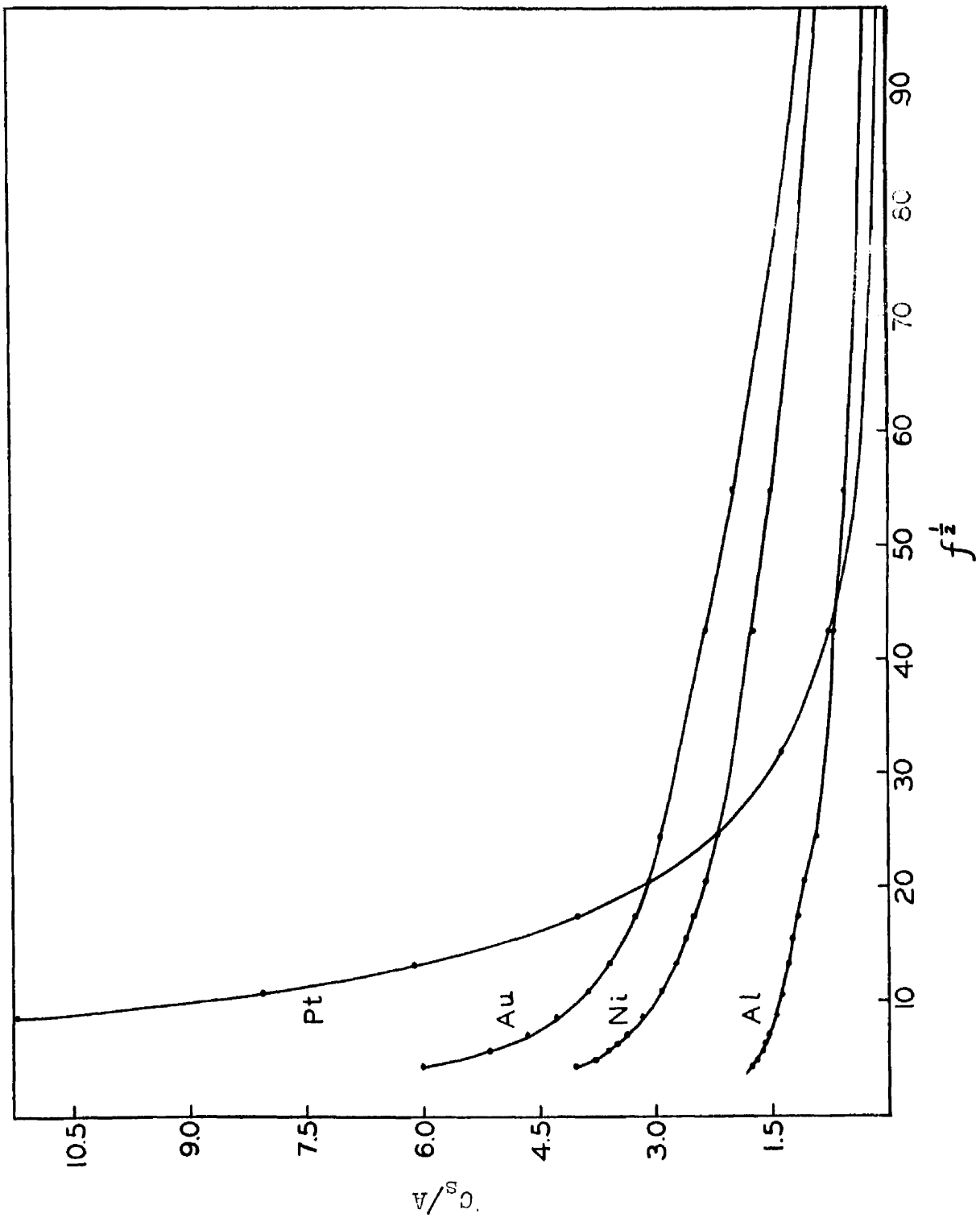
been observed previously [3,32], but a new feature noted in these observations was the more rapid decrease of capacitance with increasing frequency than occurs for other metals. This is easily seen in figure 7.

An analysis of these experimental results according to the Jaffé theory will be given in Chapter V.

FIGURE VII

CAPACITANCE VS SQUARE ROOT OF FREQUENCY

FOR KCl SOLUTION WITH SEVERAL ELECTRODES



CHAPTER III

D.C. MEASUREMENTS

Measurements on liquids in the dielectric and the intermediate range were made by dc methods. In general, a voltage was applied to the liquid between the electrodes of a cell, and the time dependence of charging current was studied. In cases where it was applicable, a voltage was removed from the electrodes and the discharging current observed. Apparatus suitable to the systematic investigation of polarization effects in a rather wide range of conductances had to be selected and assembled. The experiences encountered in the prior study of electrolytic solutions, and the work done earlier by Jaffé and LeMay [22], proved to be of great value.

A. The Conductance Cell for D.C.

The conductance cell used throughout the dc measurements was similar in general appearance to that used in the ac measurements on electrolytes. A good comparison of the two cells might be given by saying that geometrically they were alike but electrically they were quite different.

Figure 8 is a photograph of the ac cell. Description will be given of those features which are of particular interest.

1. Shielding To protect from the effects of stray fields, the sensitive central electrode and its lead were surrounded by metal shielding consisting of: the upper plate, A; the container, B; a shield plate, C; a cylindrical guard for the lead and support to the central electrode, D; the guard ring, E;

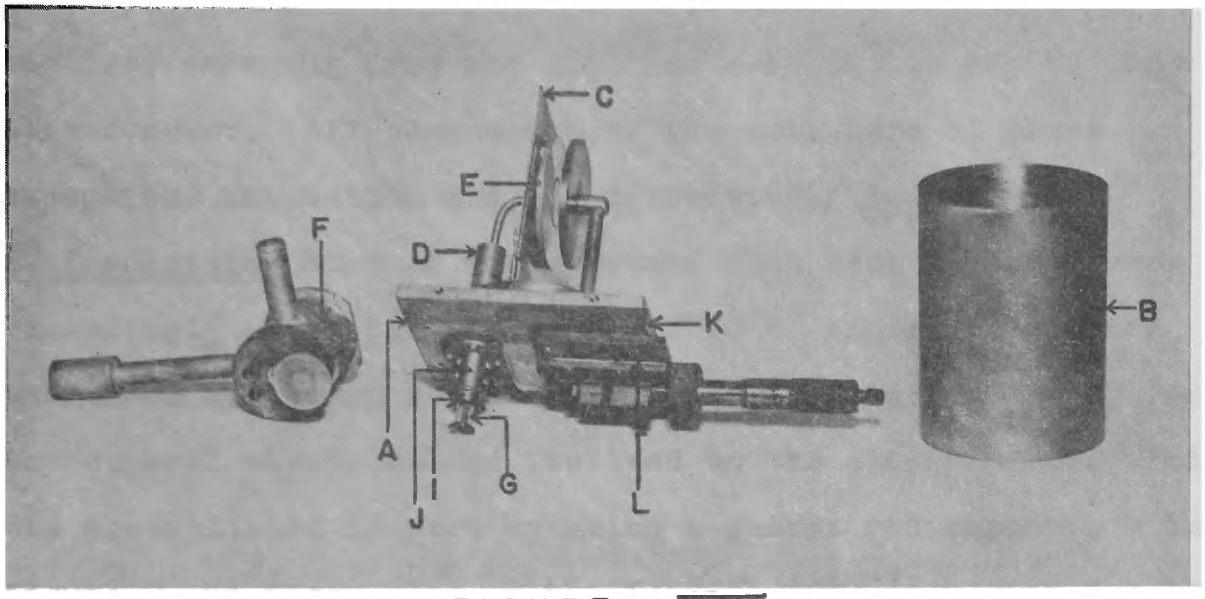


FIGURE VIII
CONDUCTANCE CELL
FOR DC

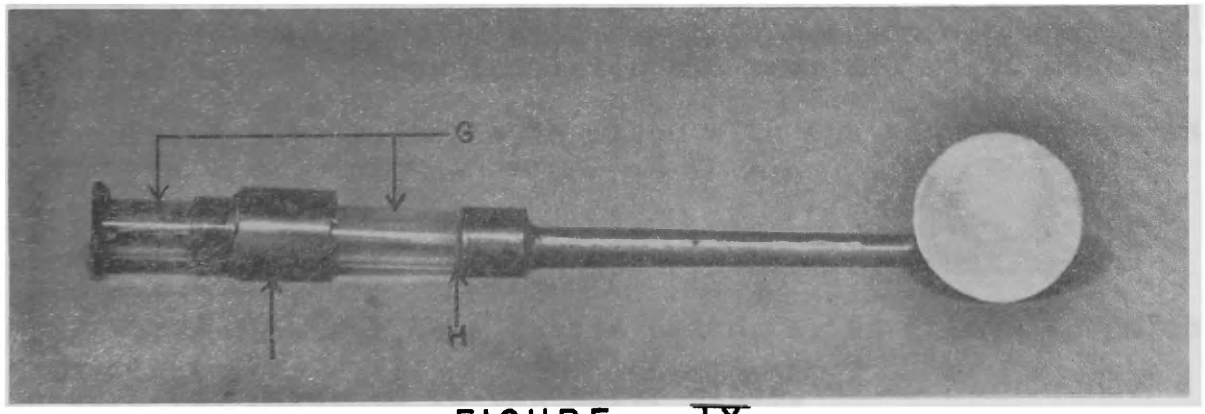


FIGURE IX
CENTRAL ELECTRODE

and the connection chamber, F, which when assembled shields the lead emerging from the cell the rest of the way to the electrometer. All components of the cell were of brass except the insulation and the micrometer.

2. Insulation Some of the currents that were measured were exceedingly small (in the order of 10^{-16} amperes). It was therefore necessary to have particularly good insulation for the central electrode and its lead to the electrometer. This was accomplished in part by using a quartz rod support, G in figure 8, to serve also as the feed-through insulator for the electrometer lead. The support rod of the central electrode was machined to a female slip fit for the quartz tubing and soldered to it with "cerroseal" solder. This joint can be seen as H in figure 9, which is a photograph of the central electrode and its supporting and insulating structure. In figures 8 and 9, one can also see the collar, I, which is soldered to the quartz insulator and provides rigid metal for holding the electrode in place with the adjusting screws in J.

High voltage insulation was provided by mounting the micrometer dovetail on a lucite plate, K, in figure 8, which in turn was fastened to the upper plate.

The remainder of the insulation was provided for by using a lead from the cell to the electrometer which was as short as possible (about 3 inches). This lead passed through the connection chamber, F, directly to the electrometer with no support. When assembled, the lower flange of the

connection chamber is screwed to the upper plate and a 25cc pyrex bulb of P_2O_5 is attached to the short brass fitting that can be seen on F in figure 8.

The upper plate was fastened rigidly to the laboratory table and served as a supporting structure for all the rest of the assembly except the container which was supported by a shelf which slipped into place at the proper height.

3. Electrode separation Provision for electrode adjustment was incorporated by having the high voltage electrode mounted on the micrometer-driven dovetail, L.

This cell was found to be entirely satisfactory except in two respects. First, it was not completely sealed against the atmosphere - this allowed loss of liquid by evaporation, and probably a contamination of the liquid by the atmosphere. Second, the volume was rather large (about 400 cc's) -- this necessitated the preparation of relatively large quantities of sample.

The important dimensions of the electrodes were as follows:

Radius of the central electrode - - - - 1.024 cm

Inner radius of the guard ring - - - - -1.078 cm

Effective area of the central electrode-3.45 cm^2

B. Purification of Liquids

Preparation of the liquid samples for measurement consisted principally of repeated distillation of the liquid and washing of all vessels and the cell with each batch of distillate until preliminary tests of conductivity indicated that further distillation was unprofitable.

It should be remarked that chemical purity of the sample was not the most important criterion of purity here. The impurities that need to be removed are those that contribute to the conductance rather than isomers that do not separate by distillation.

The distillation apparatus consisted of a Corning Glass #4320 boiling flask, a Scientific Glass # J-1084 Widmer distilling column with air jacket, a Scientific Glass # J-1161 vacuum jacketed distilling head fitted with a 0-350°C thermometer graduated by tenths, a Corning Glass # 2640 Fredericks water cooled condenser, and a Corning Glass # 4320 500 cc receiving flask.

Heat was supplied by an electric heater and controlled by varying the voltage supply with a Variac. Two different heaters were used. The research was begun with a 550 watt Precision Scientific heater used to heat an oil bath in which the boiling flask was immersed. Later a 1000 watt Glass Mantle heating unit was procured. The latter was much more satisfactory especially for distillation of liquids of higher boiling point.

The stock liquids which were to be processed were of "analytical reagent" grade according to the various manufacturers from whom they were purchased.

C. Experiments in the Dielectric Range

Measurements on liquids in the dielectric range were performed for the following purposes: first, to master the techniques of experiment and to test the equipment in a range

of conductance that had been previously measured; second, to investigate the dependence of polarization on electrode separation; third, to verify previous work that had been done with a cell that did not have guard ring advantages [22,23]; and fourth to investigate the effect of gamma radiation of intensity greater than had been used previously.

The liquid chosen for the investigation was hexane since experience by Jaffé had shown that it would be ideally suited to efforts toward the above objectives.

1. The Electrometer The currents in this range were measured with a Lindemann electrometer mounted on the stage of a microscope. The position of the microscope was such that the electrometer could be connected directly by the short lead from the cell described in part A of this chapter. This lead passed through the connection chamber tube from the quartz insulation of the cell electrode to the quartz insulation of the electrometer. Electrical connections were made with silver solder to the cell electrode and by binding post to the electrometer needle.

The electrical diagram of the apparatus for these measurements is given in figure 10. The system was quite simple and conventional and very little explanation need be given. One special feature of design was the grounding switch S_1. This switch was made as part of the connection chamber shown in figure 8. It had platinum to platinum contacts and was screw controlled by an external knob on the cover of the connection chamber. It proved to be quite satisfactory for the delicate

operation of grounding and ungrounding the electrometer needle circuit. The electrometer voltage supply unit was the standard Lindemann voltage supply unit manufactured by the Cambridge Instrument Company.

The Lindemann electrometer indicated the potential of the needle as a deflection which was read in the microscope. It was calibrated by switching S_2 to a suitable calibration potential and observing needle deflection. This calibration was performed before and after each series of data was taken. The sensitivity of the electrometer was varied by adjusting the supply potential.

The capacitance of the system was determined for each condition of operation: i.e., for the full range of electrode separation with the liquid under study in the cell. This was done with a General Radio R.F. capacitance Bridge Model 1612-A. Values of cell-electrometer capacitance ranged from 25 to 40 micromicrofarads.

The image of the electrometer needle was viewed in the microscope, superimposed on an eyepiece scale. Using a stop watch, determinations were made of the time deflection rate of the electrometer immediately after undergrounding the needle with S_1. From the deflection rate, the voltage sensitivity, and the capacitance the current was readily calculated. Currents measured with this system ranged from 5×10^{-16} amperes to 6×10^{-13} amperes.

Before commencing any measurements, a check was always

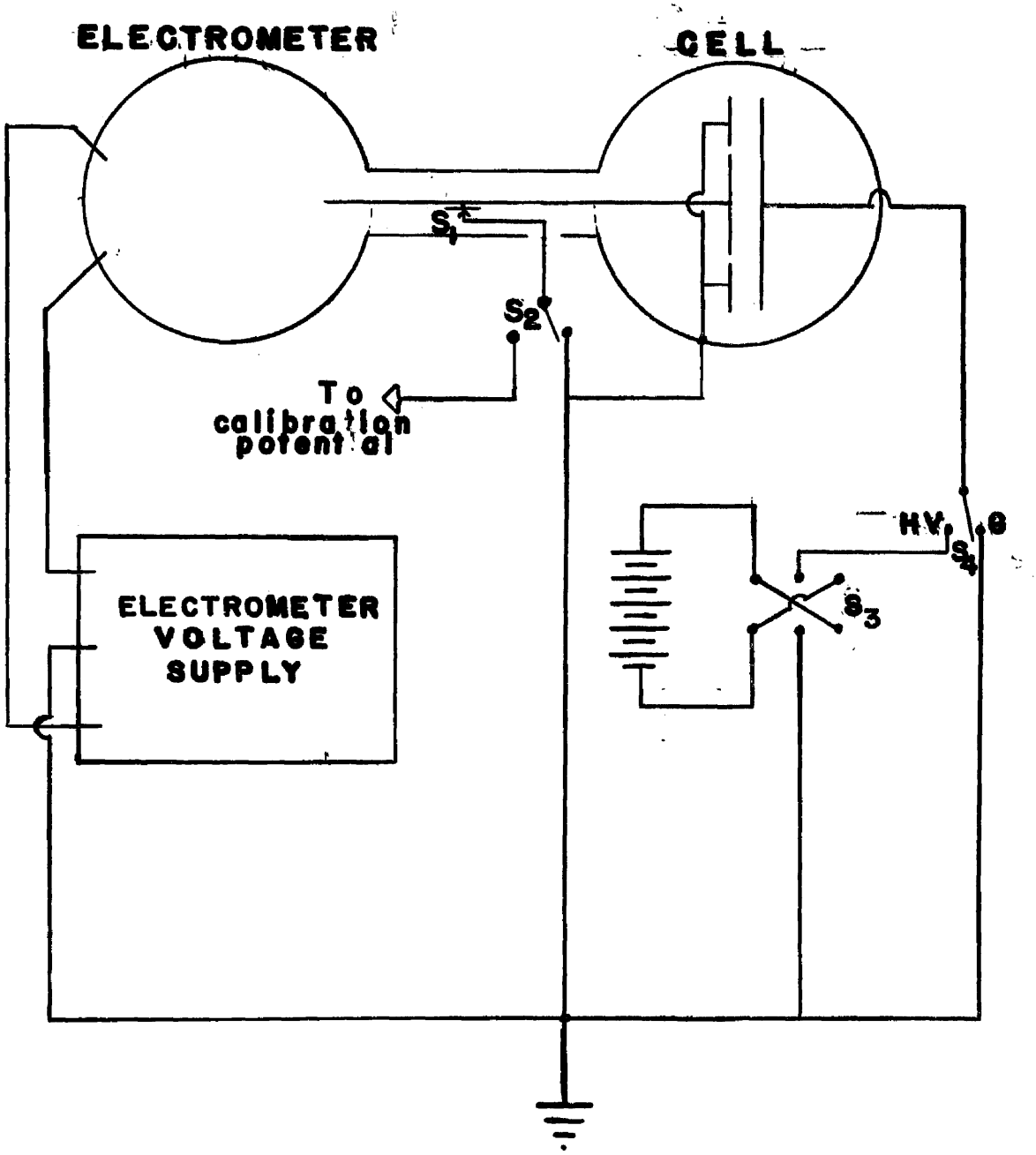


FIGURE 10.

DIAGRAM OF ELECTROMETER AND CONDUCTANCE CELL CIRCUIT

made of the leakage rate of the system. To do this a small potential was applied to the needle circuit from the calibration potential. Thus charged, the needle was left "floating" by opening S_1. If the needle charged leaked off at a rate of 10% per minute or less, the insulation was deemed satisfactory.

In this connection, there is another leakage check. If the needle circuit were "floated" at ground potential, it should have remained there indefinitely regardless of the leakage as long as there was no part of the system at any potential other than ground. This was never the case - - left undisturbed for a sufficiently long time the needle always attained an equilibrium potential of 0.14 volts. This is explained by noting that the Lindemann electrometer is made within an aluminum housing while the cell and all shielding were made of brass. It was thus inevitable that there should exist a contact potential, namely, that of aluminum-brass. When the leakage was not sufficiently low for reliable measurements, a drift to contact potential could always be noted.

For high precision with very small currents, some drift (such as that due to contact potential) was bound to be present. It can be measured and corrections for observations can be calculated. The drift in these measurements due to the electrometric system was so small that corrections were applied only in a few extreme cases.

2. Measurements on Hexane Without Radiation In making observations on hexane, it should be stated that it was not

one of the aims of this research to render the conductivity as low as possible, nor to establish conductivity values for extreme purity. As Jaffé discovered, polarization effects practically disappear for extremely pure hexane [10]. This observation was confirmed by LeMay [22,23]. Further, it was not practical to attempt routine measurements of currents smaller than 10^{-15} amperes because of prevailing humididity conditions in this climate. Since it was the polarization effects being studied, it was decided to make measurements on hexane of a purity such that the polarization was still appreciable but such that the currents were as low as practicable.

Samples of hexane having specific conductivity, K, in the range of 10^{-18} (ohm cm)$^{-1} < K < 10^{-17}$ (ohm cm)$^{-1}$ were used. Of course, there is little meaning to specific conductivity for this kind of conduction since the currents do not obey Ohm's law. The value of K obtained from experiment depends not only on the voltage range but also on the time elapsed after application of voltage. Wherever stated in these results, values of K have been calculated with data taken 1 hour after the application of voltage and are figured from the average slope of the voltage-current curve for a range of field between 1000 volts/cm and 2000 volts/cm.

Most of the measurements were of current vs time after the application to or removal of a voltage from the high voltage electrode. Application or removal of the voltage

was accomplished by switching S_4 in figure 10. It will be seen that "removal" implies immediate grounding of the electrode. The polarity of the high voltage was controlled by S_3 in figure 10.

The sequence of measurements for a single series was as follows:

(a) The electrometer voltage supply unit was turned on (unless it was still on from earlier use).

(b) A voltage was applied to the high voltage electrode. The polarity of this voltage was opposite to that with which the series was to commence.

(c) Checks of leakage and calibration were made.

(d) After an elapsed time equal to the duration of a series, the voltage was removed from the high voltage electrode, and the apparatus left undisturbed for about fifteen minutes.

(e) Switch S_3 was reversed and S_4 closed in the high voltage position.

(f) Within a few seconds after step e, the first reading of current was commenced by opening S_1 and determining the deflection rate. S_1 was then closed, grounding the electrometer needle.

(g) At predetermined time intervals after application of the voltage (step e) successive determinations of deflection rate were observed as in step f. This was continued until the current was practically

constant.

(h) After steady current was established, S_4, was switched to the ground position.

(i) As soon after grounding S_4 as possible, deflection rates for the discharge currents were determined as for the charging currents in steps f and g. This was continued until no deflections occured upon opening S_1.

(j) S_4 was reversed and S_3 switched to high voltage position for measurements of the opposite polarity.

(k) Steps f,g,h, and i were repeated with the opposite polarity.

Such series were made at various values of applied voltage for several electrode separations, and with several samples of hexane. The results are given in section E of this chapter.

3. Measurements on Hexane with Radiation As pointed out in the Introduction there have been many investigations of conduction through liquids under the influence of ionizing radiation. In this project some of the measurements were made with an intensity of radiation greater than had been used previously. The results of the high intensity radiation were straightforward, and quite what would be expected. It was, therefore not necessary to extend this phase of the investigation.

Two sources of radiation were used. The smaller was a milligram radium source placed outside of the cell, 5 cm

from the center of the space between the electrodes. This source was used to provide radiation of intensity within the range used in earlier investigations by LeMay [23]. The other source was a 100 millicurie source of Co^{60} borrowed from the L.S.U. Radiochemical Laboratory. The cobalt source was encased within a heavy lead vault containing a collimating aperture, as shown in figure 11. The radioactive material was at a distance of 25 cm from the center of the cell.

Measurements of current for the experiments with radiation were performed in the same manner as for those without radiation except that the sensitivity of the Lindemann electrometer was reduced according to the larger currents observed.

Series of measurements were made on samples without radiation, using the smaller source, and using the larger source. The results are given in section E of this chapter.

D. Liquids of Conductivity in the Intermediate Range.

1. Current Measuring Systems In order to conduct the investigations on liquids having conductivity in the range intermediate between that of aqueous solutions (including water) and hexane, it was necessary to modify the current measuring system to measure the larger currents. Two methods were used.

(a) Capacitor padding of the Lindemann electrometer. For some of the measurements the Lindemann electrometer was padded with one of three capacitors depending on the range in which currents were to be measured. These were 100, 200,

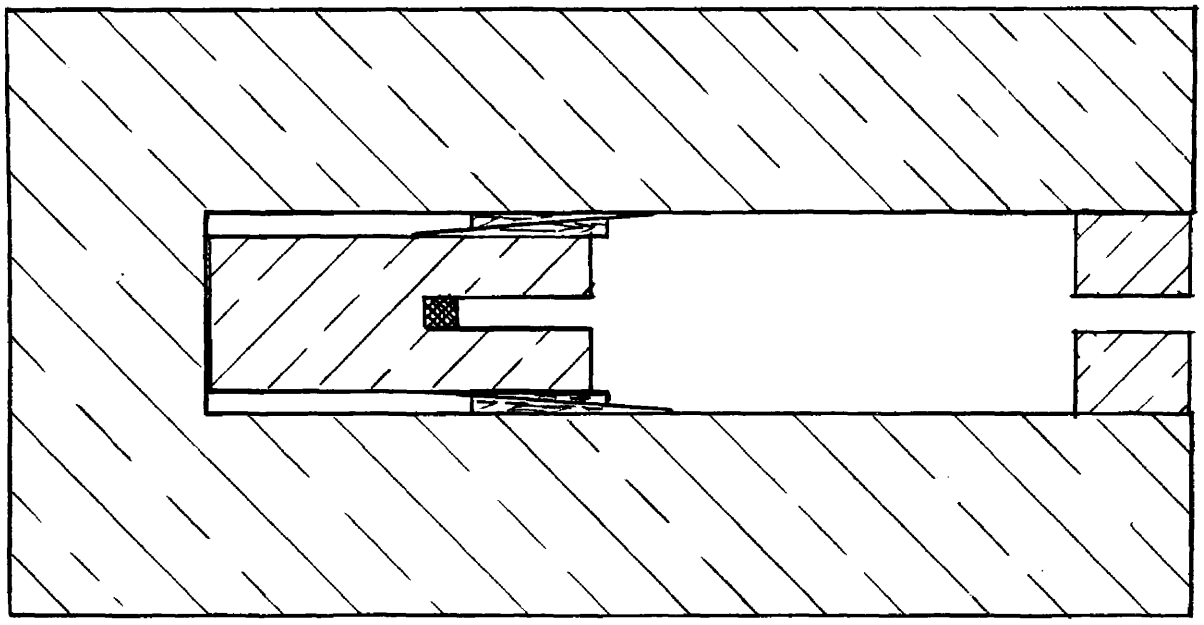


FIGURE XI

DIAGRAM OF VAULT
FOR Co^{60}

and 500 micromicrofarad "Glassmike" capacitors. Their use extended the current range of the electrometer up to 10^{-10} amperes.

It might well be asked why a cumbersome electrometric system of charging rate was used for currents of the order of 10^{-10} amperes. The reason was that provisions were made to observe also the much smaller discharge currents that were anticipated. This was to be done by switching out the capacitor and adjusting the sensitivity of the electrometer to a suitable value. However, for the liquids investigated in the intermediate range, discharge currents entirely escaped detection. Indeed, as soon as attempts to measure the discharge currents proved futile, plans were commenced to arrange another current measuring system.

(b) D.C. Amplifier System Most of the currents in liquids in the intermediate range were measured with the dc Amplifier of a Leeds and Northrup, Knorr-Albers Microphotometer Model 6700-A1 [37]. The output of the microphotometer amplifier was fed to a Leeds and Northrup Speedomax recorder model 6700-P2. The currents were continuously recorded on the recorder chart paper which was driven at a standard chart speed of 4 inches per hour. Thus, an automatic plot of current versus time was obtained.

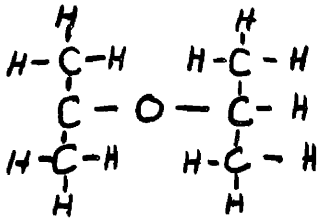
Figure 12 is a diagram of the system as used with the amplifier. The only modification made on the amplifier were the installation of a coaxial cable connector, PL, and a switch, S_1. The central electrode of the conductance cell

was connected to the amplifier by means of a coaxial cable.

Input current flows through the two 20 megohm resistors, the cathode resistors of the last stage, and to ground through the recorder. The RI drop thus produced provides an input voltage for the grid of the first state. This voltage is amplified causing the current to change in the last stage until the negative feed back from its cathode circuit nearly returns the grid of the first stage to its initial potential. Under these conditions the relatively large cathode current of the last amplifier stage is proportional to the input current and easily drives the Speedomax recorder.

Although the central electrode is not at ground potential, it remains sufficiently near it for the guard ring to retain its effectiveness.

2. Measurements on Isoproply Ether Isoproply ether was chosen as one of the liquids to be investigated in the intermediate range. The structural formula is



It has a conductivity in the order of 10^{-14} (ohm cm)$^{-1}$, a factor 10^4 greater than hexane and 10^8 less than water. Of all the liquids having about the same conductivity as isopropyl ether, it was selected because of the following considerations:

(a) availability of samples commercially.

(b) relative ease of purification by distillation.

(c) sufficiently low rate of evaporation under standard

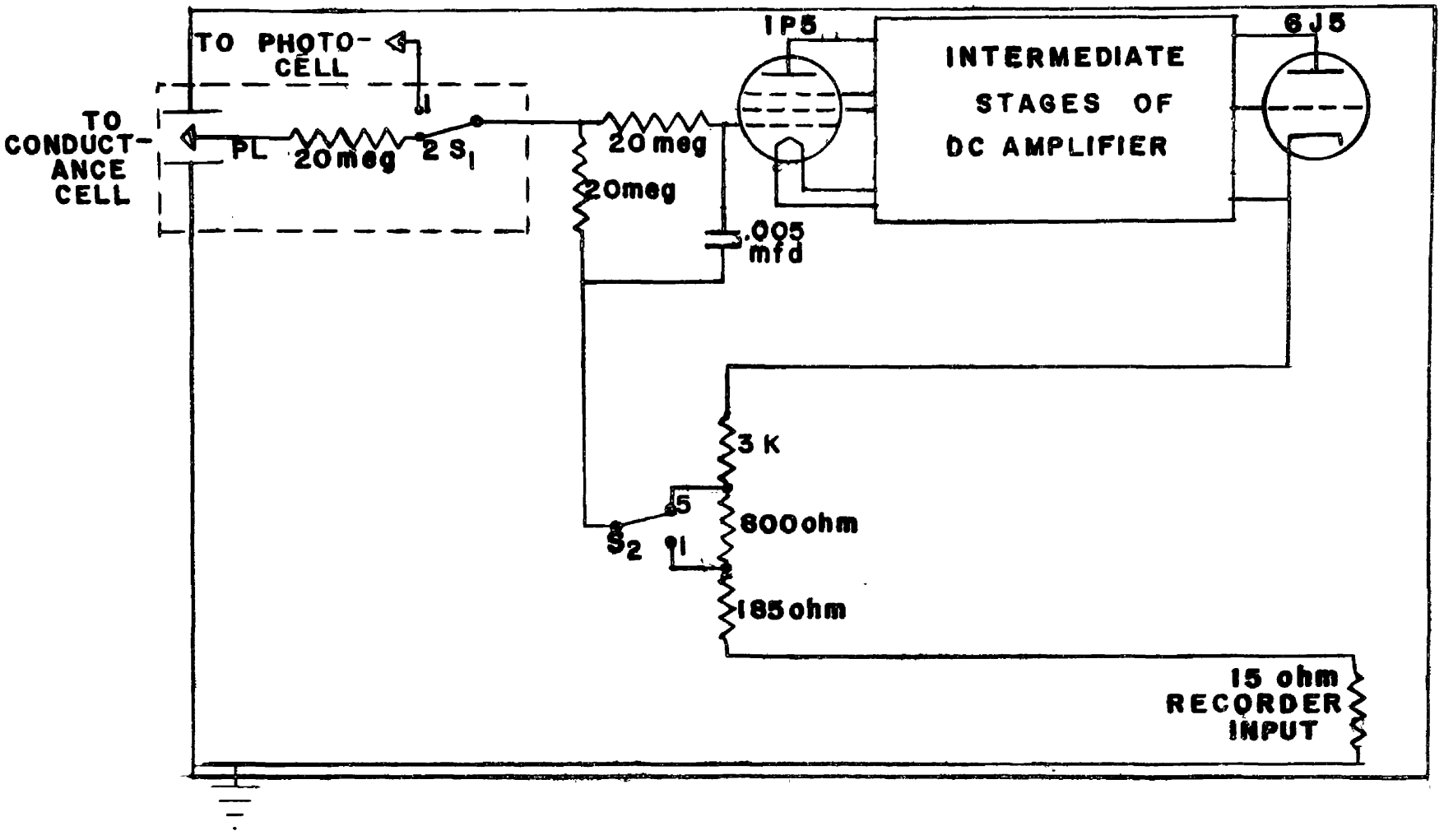


FIGURE XII

DC AMPLIFIER

SYSTEM

conditions of temperature and pressure.

(d) chemical inertness to brass electrodes and to cell.

One factor that was not known in advance was that under the application of an electric field some chemical change occurs in the liquid. It is believed that the field renders the C-O-C bond unstable so that some of the molecules split yielding propane derivatives. Whatever the process, two effects were noted in the investigations. First, there was a gradual increase in conductance for every sample; and second, upon redistillation of a batch upon which measurements had been made, fractions (amounting to about 10%) boiled off well below the boiling point of isopropyl ether.

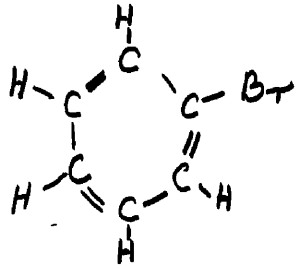
This, however, made little difference in the polarization study. As in the other cases, these measurements were concerned with correlating the general pattern of polarization and not with the establishment of precise values of the conductivity of any substance.

Fundamentally, the procedure of observation was the same with isopropyl ether as for the hexane measurements described in section C part (2) of this chapter. In those measurements made with the Lindemann electrometer the routine was the same. For the measurements made with the dc amplifier system, the details differed in that point by point observations were replaced by continuous recording.

Series of measurements were made of current vs time for various voltages and for various values of electrode separation on each of several samples of liquids. The results are given

in section E of this chapter.

3. Measurements of Bromobenzene Between the range of conductivity of isopropyl ether and that of water, there remained a gap in which no data was available with which the Jaffé theory could be tested. Bromobenzene was thought to be a suitable liquid in this range since it has a conductivity in the order of 10^{-10} $(\text{ohm cm})^{-1}$, which is 10^4 greater than isopropyl ether and 10^4 less than water. The structural formula for bromobenzene is



A sample of bromobenzene was purified and measurements were attempted of current vs time following the application or removal of a voltage. The currents were to be measured in the same manner as those on the isopropyl ether except that the amplifier sensitivity was adjusted to correspond to the larger conductance.

Using the same range of applied voltage as had been used in all other dc measurements, it proved to be impossible to make current measurements. The current fluctuated wildly and erratically as soon as the voltage was applied to the cell. The behavior suggested rapid and intermittent breakdown and healing of an electrolytic film. Accordingly, the applied voltage was reduced to lower and lower values until satisfactory performance was finally achieved with the unusually low value of 1.5 volts.

At this point, the electrodes were removed, examined visually, re-ground, and polished before continuing with the investigations. The examination showed only a faint hazy appearance on the surface. No attempt was made at a critical analysis of the surface. A fresh sample of bromobenzene was prepared and a second attempt was made to obtain data. This time an applied voltage of 1.5 volts was used throughout, and no unstable performance was encountered. The results, however, were somewhat unusual. Not only were the current vs time curves for the two polarities unsymmetrical, but one of them (high voltage electrode of negative polarity) showed an increasing current with increasing time for which it is difficult to account.

Every effort had been made to avoid asymmetry in the system. The electrodes were all machined from the same stock of brass. It was believed that the asymmetry was due to the electrical history to which the surfaces had been subjected since they had been ground and polished. Therefore, the electrodes were again removed, re-ground, and polished; and preparations were made for a third run on bromobenzene. This time the polarity sequence of applying voltages to the cell was just exactly reversed from the sequence that had been used in the previous run. It was reasoned that this might reverse the direction of asymmetry of the current vs time curves.

The third run on bromobenzene yielded the same results, qualitatively, as the second run. The direction of asymmetry

was not reversed.

The results obtained in these runs are given in section E of this chapter and are discussed briefly in Chapter VI.

E. Results of the D.C. Measurements

In all results, except those obtained with bromobenzene, there is straightforward agreement with the earlier work of Jaffé and LeMay. Even the bromobenzene does not show a disagreement but rather an indication that other effects strongly interfere with observation of the polarization.

The results of the three ranges will be presented in this Chapter and the agreement between them and the theory will be discussed in Chapter V.

1. Hexane Figure 13 shows the results obtained on a sample of hexane of conductivity 1.98×10^{-19} $(\text{ohm cm})^{-1}$. This represents typical behavior of current vs time for charging and discharging with both polarities. As expected the currents begin to fall off rapidly following the application of a voltage to the liquid. As time progresses the rate of decrease becomes less rapid so that after about ten minutes it has nearly reached an equilibrium value. The discharge currents also begin with a rapid decrease and then approach an equilibrium value of zero.

In these measurements on pure hexane there was no reversal of direction in the discharge currents. However, this is not general. Reporting on discharge currents in solutions of lead oleate in hexane, Jaffé and LeMay refer to measurements in

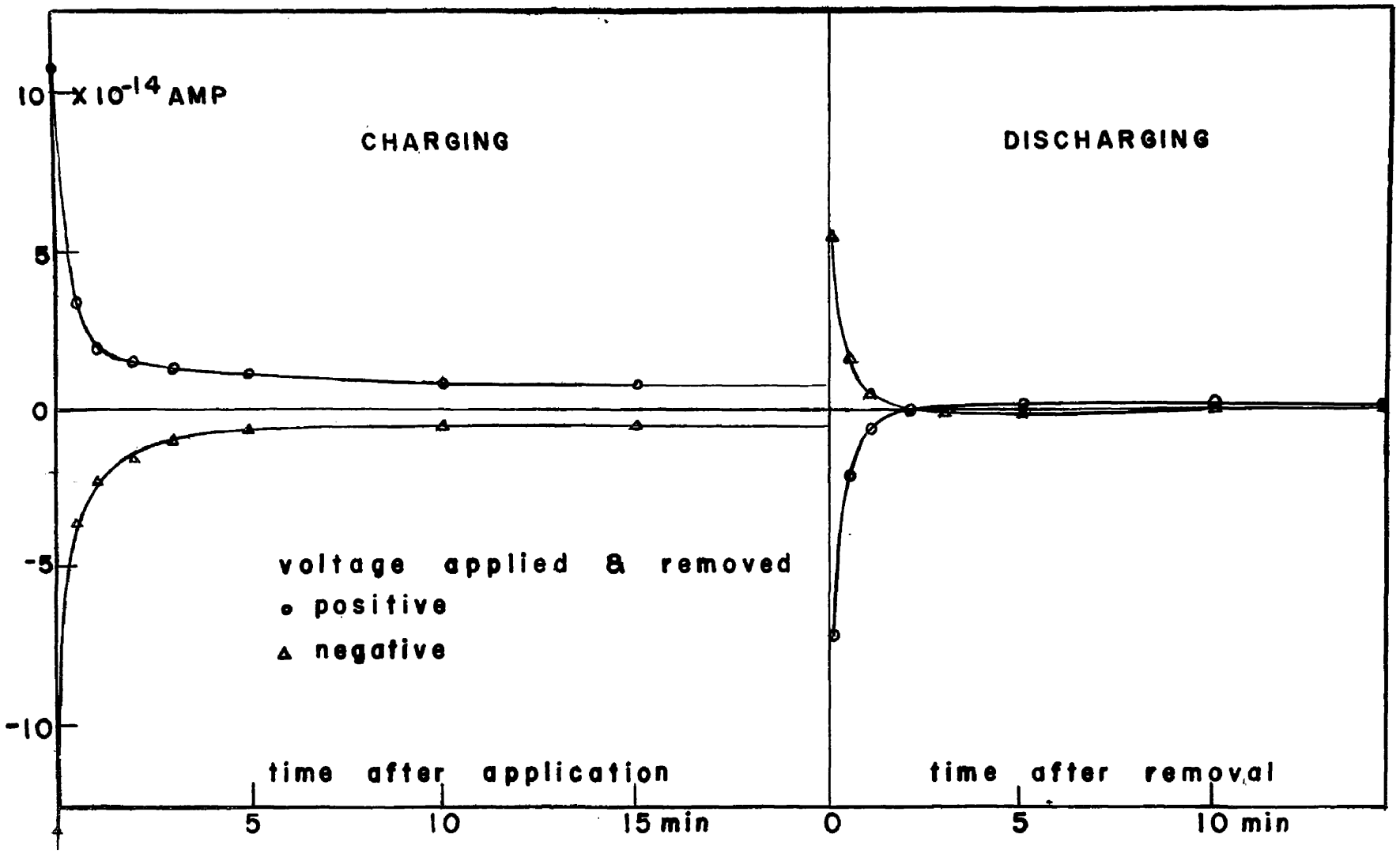


FIGURE XIII
CURRENT VS TIME
HEXANE

which there is a reversal of direction of discharge currents after about 40 seconds following the removal of a voltage [22]. This point will be discussed further in Chapters V and VI.

Careful examination of the current vs time curves will in all cases show an asymmetry between the one taken with positive and the other taken with the same negative voltage. So far no completely satisfactory explanation of this has been advanced. To eliminate this asymmetry the positive and negative currents have been averaged in the analysis of the curves. The average currents for the series shown in figure 13 are plotted in figure 14 as the no radiation curves.

To observe the effect of electrode separation on polarization, the measurements given in figure 14 were taken. These are of charging currents for five series taken at different distances of electrode separation but at constant field. Since the measurements were made over a period of two days, there were changes in the conductance of the hexane during the course of the measurements.

Figure 15 is a typical example of charging and discharging current vs time with and without the gamma radiation of the 1 milligram radium source. The form of the current curve with radiation shows the presence of a growth component. After falling for a few minutes the current begins to increase and then approaches an equilibrium value which is naturally larger than the corresponding current without radiation.

The results of measurements with the 100 millicurie source of Co^{60} are shown in figure 16. Here the three curves

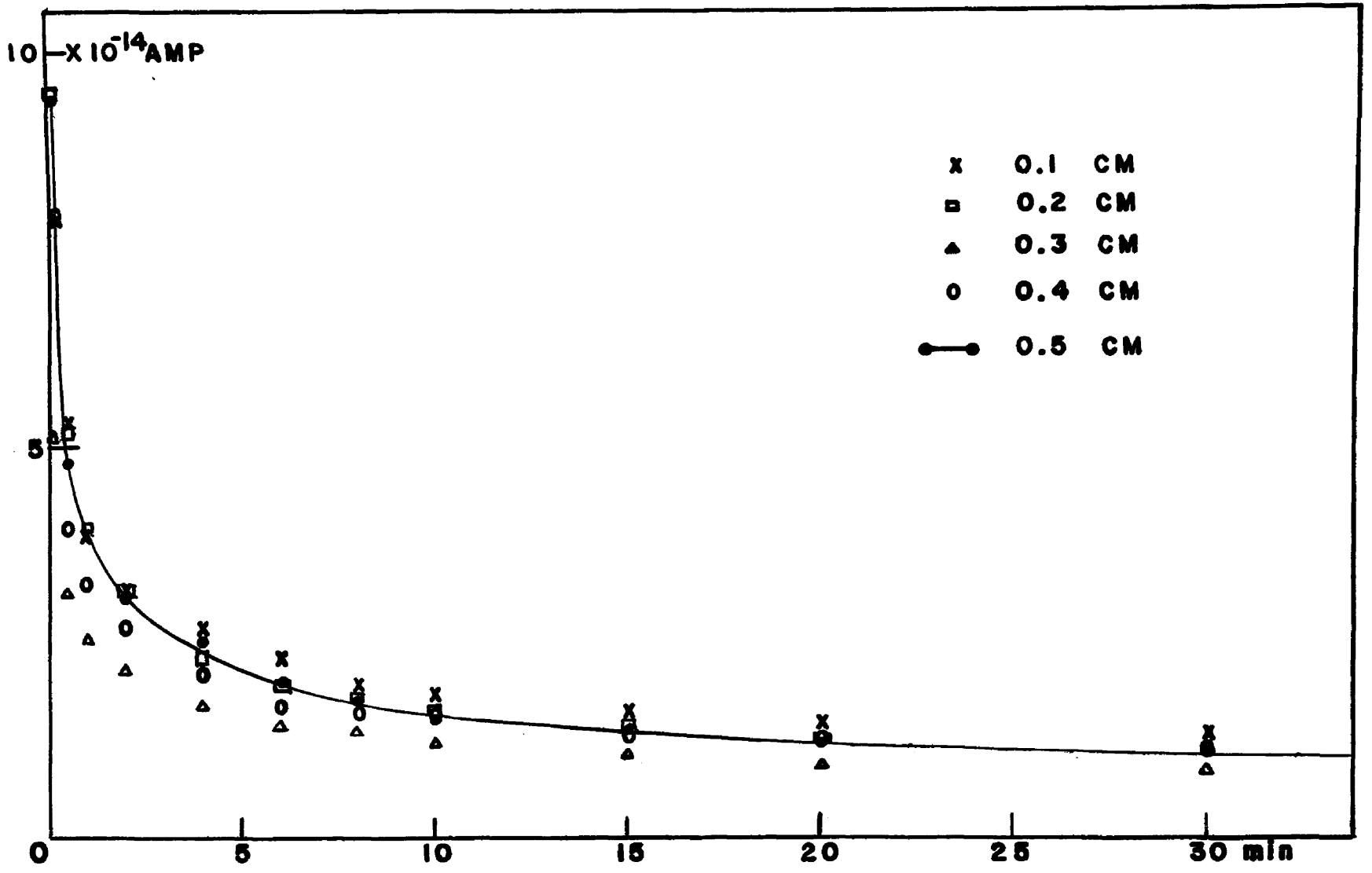
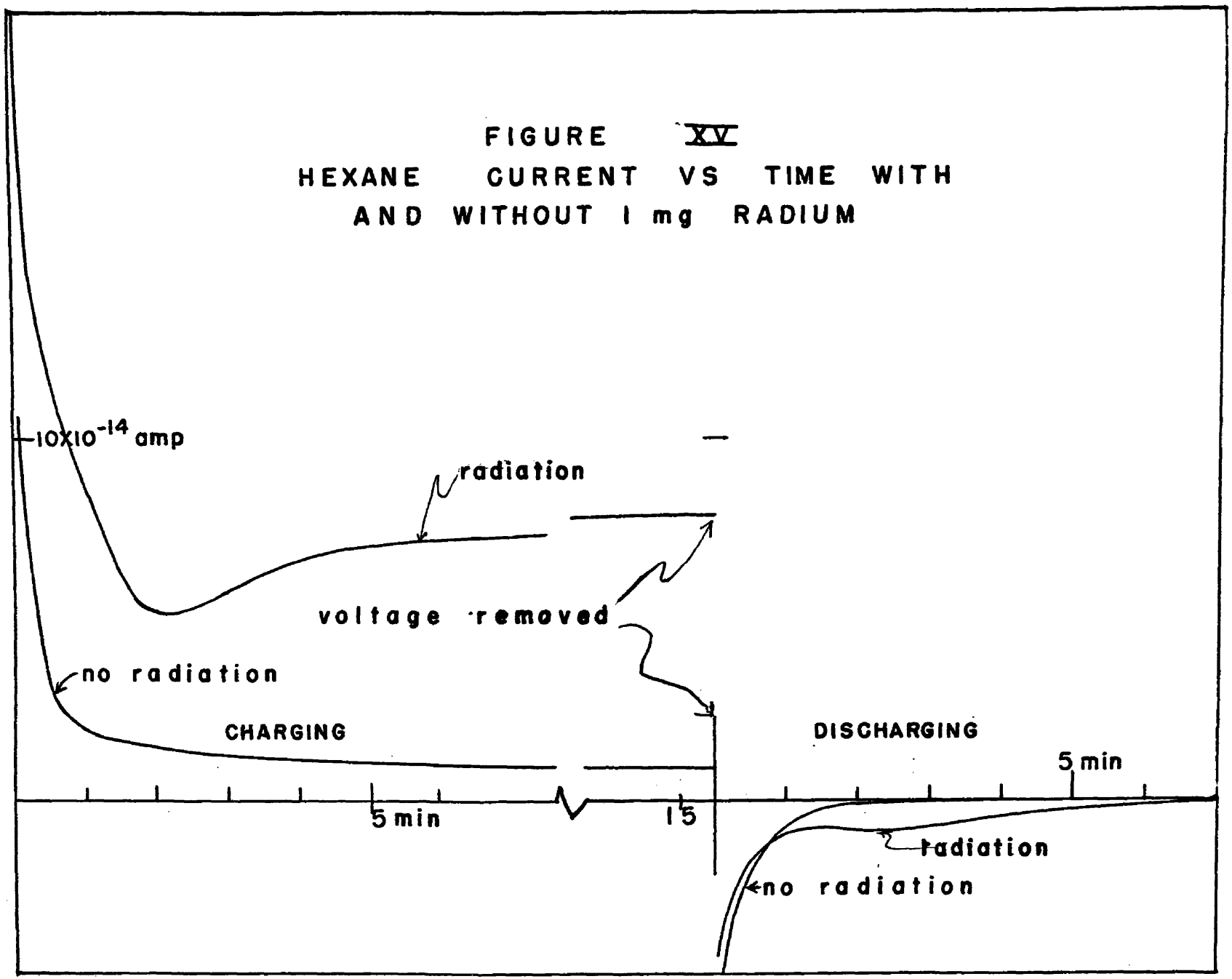


FIGURE XIV

HEXANE CHARGING CURRENT VS TIME WITH CONSTANT FIELD

FIGURE XV

HEXANE CURRENT VS TIME WITH AND WITHOUT 1 mg RADIUM



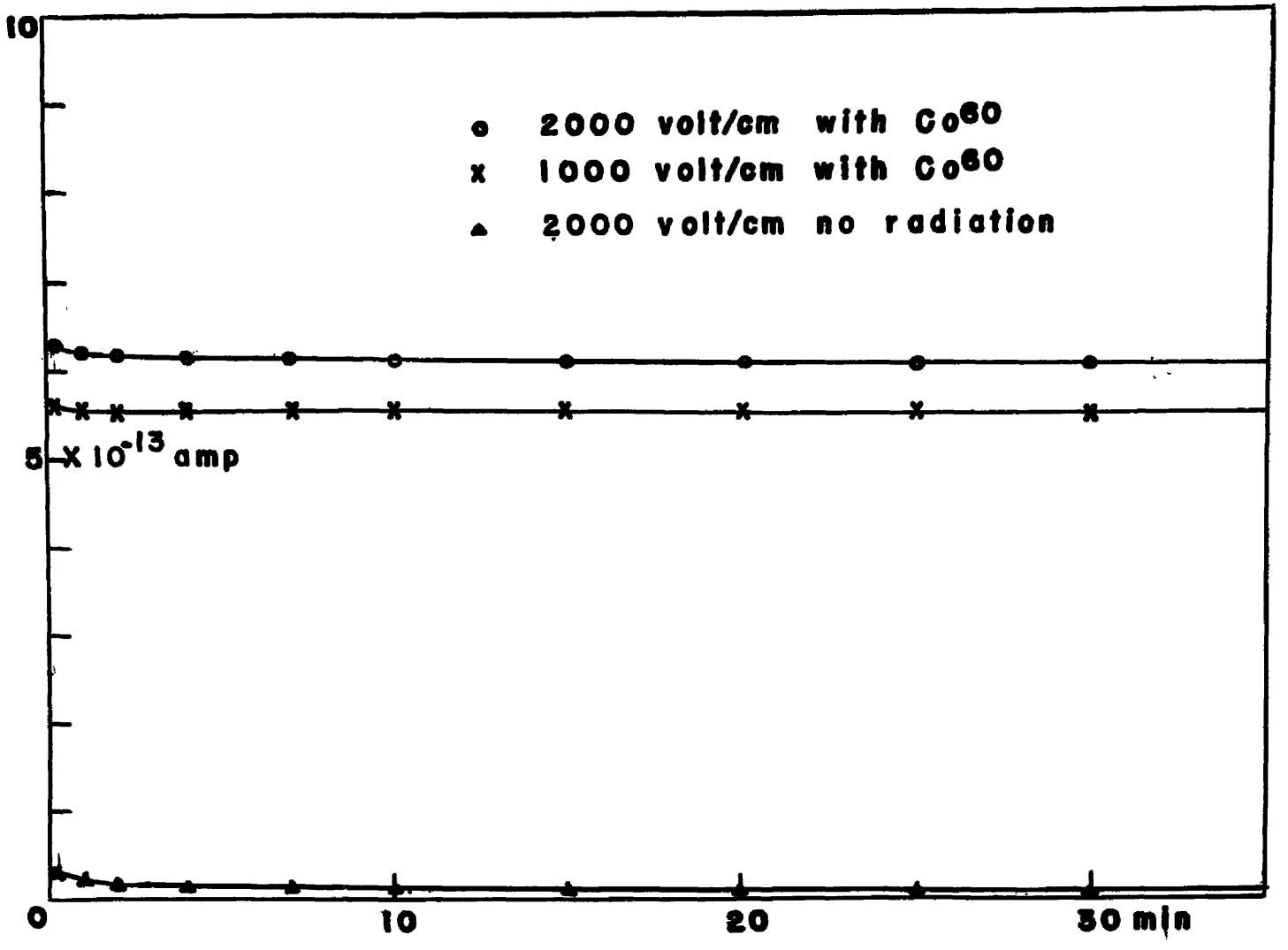


FIGURE XVI
HEXANE CURRENT VS TIME
WITH AND WITHOUT 100 millicurie Co^{60}

shown are for no radiation, radiation with a field of 1000 volts/cm, and the same radiation with a field of 2000 volts/cm. The two radiation curves are practically constant with respect to time as would be expected. Considering the currents for the two fields it can be seen that the current is mostly saturation current.

These results are further discussed in Chapter V where they are compared with theory.

2. Isopropyl Ether Figures 17 to 24 were prepared from data taken in measurements on isopropyl ether. There were two important differences between these results and those obtained on hexane. In these on ether, the current decay persisted much longer, and there were no measureable discharge currents. As in the case of hexane, there is asymmetry between the currents observed with different polarities of applied voltage. In neither hexane or isopropyl ether is the asymmetry comparable to that observed with bromobenzene.

Typical results of a single series of current vs time measurements on isopropyl ether are presented in figures 17 and 18. Figure 17 shows the curves as transferred directly from the recorder chart. The same data is re-plotted in figure 18 with the negative current reflected so that the two curves representing opposite polarities may be compared. Data analysis and comparison with theory was performed with the average currents such as that shown in the dashed curved in figure 18.

Figure 19 shows three curves for three voltages, each

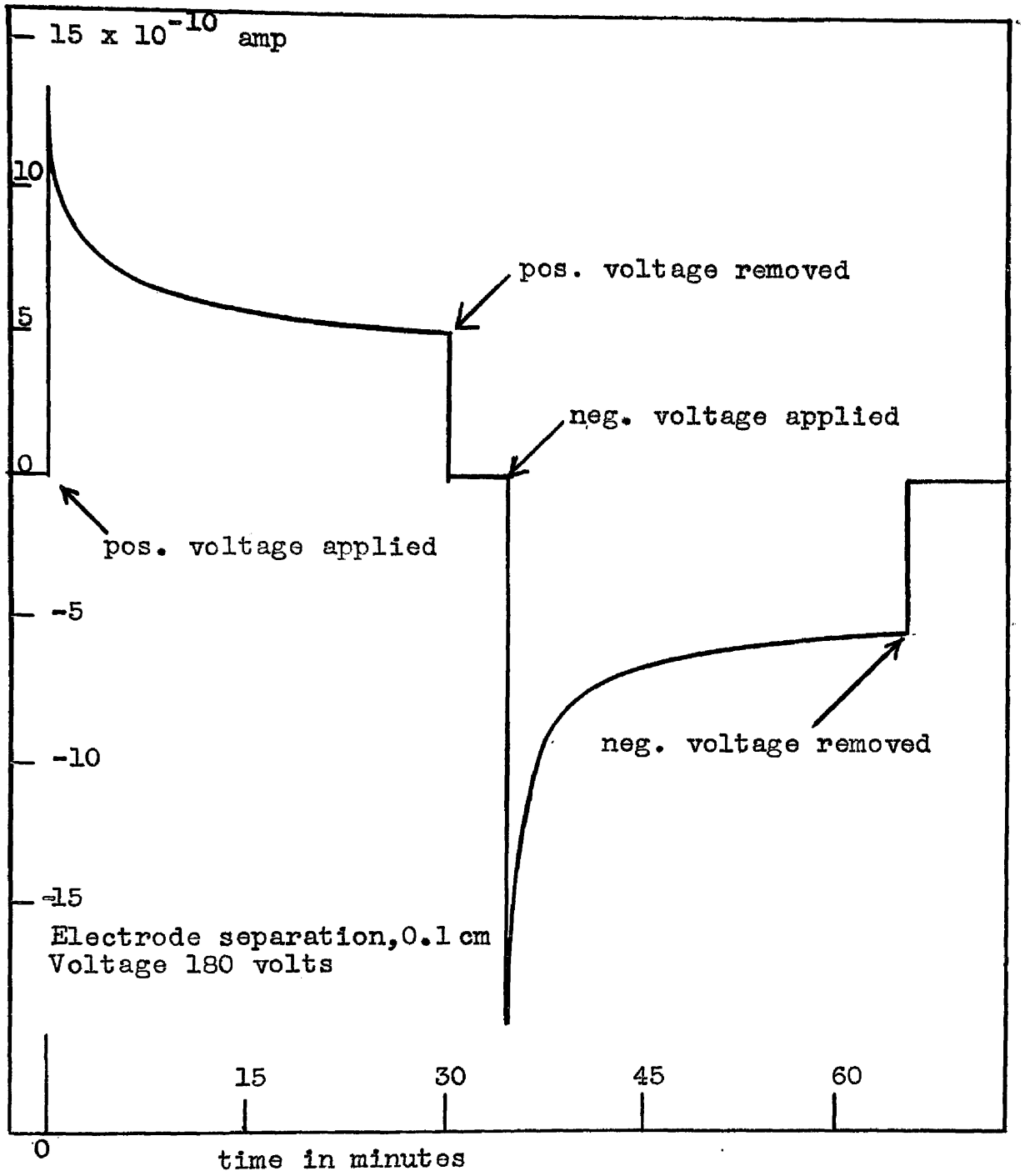


FIGURE XVII

ISOPROPYL ETHER

CURRENT VS TIME BOTH POLARITIES

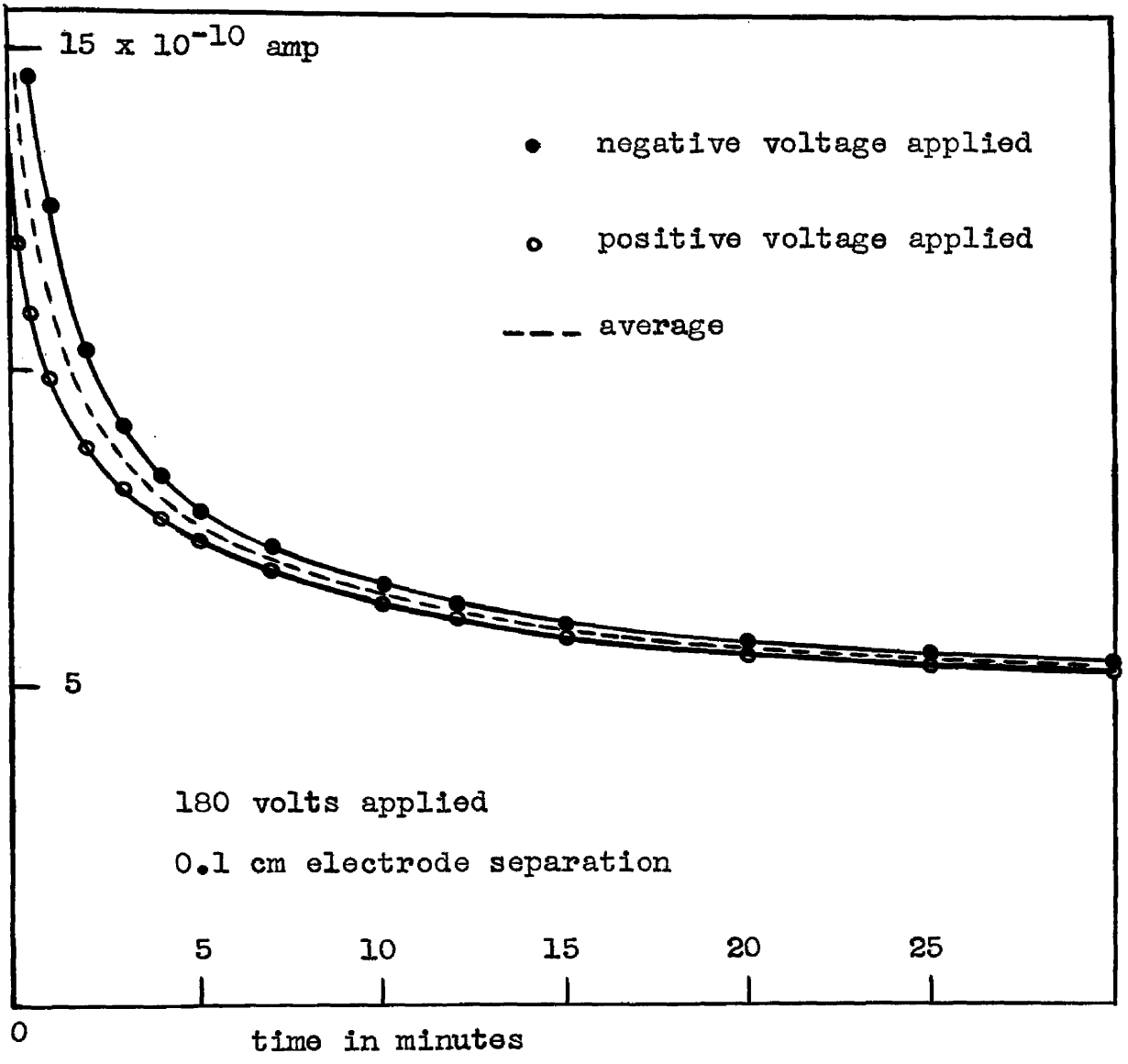


FIGURE XVIII

ISOPROPYL ETHER

CURRENT VS TIME SHOWING

BOTH POLARITIES AND AVERAGE

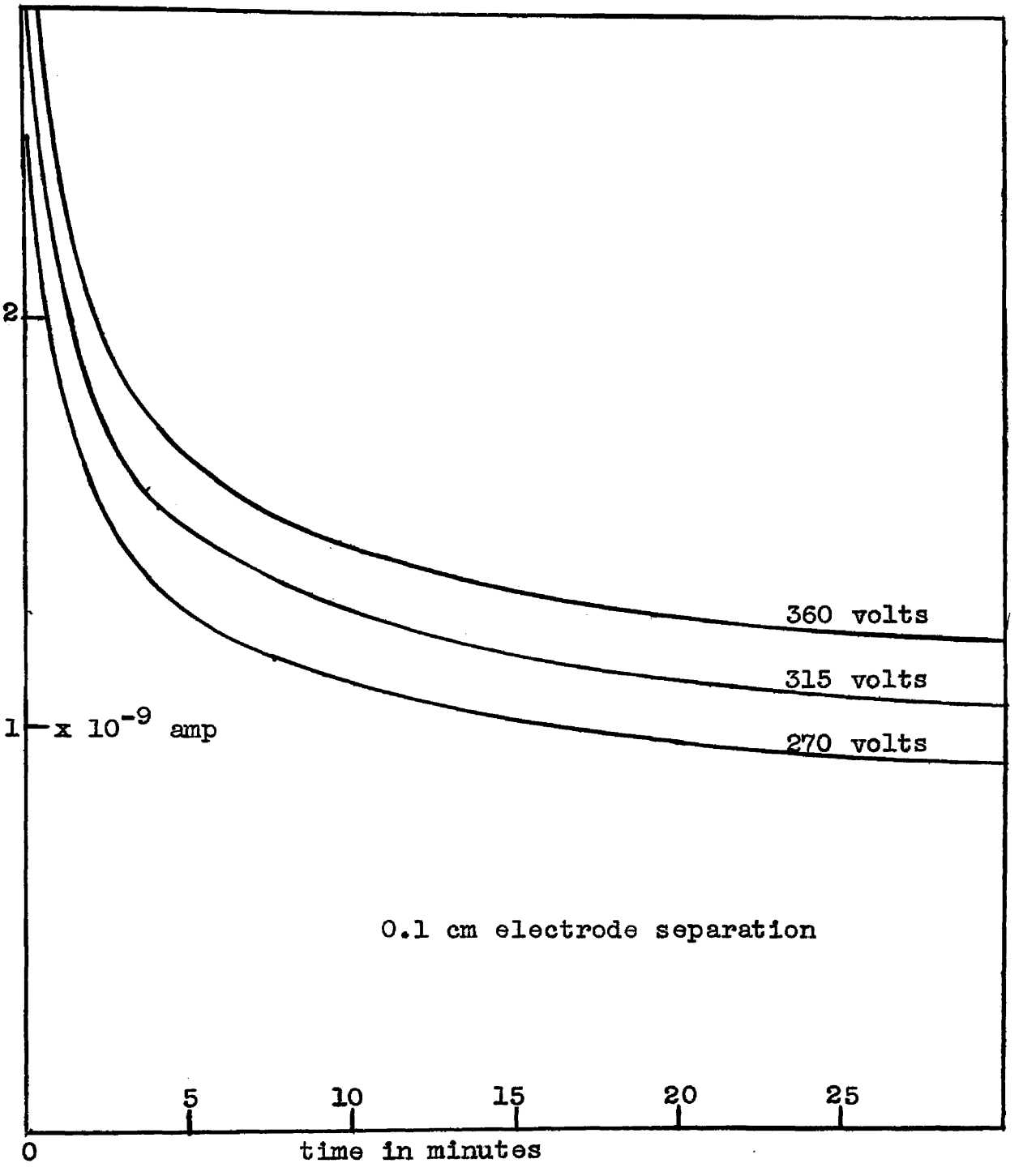


FIGURE XIX

ISOPROPYL ETHER

AVERAGE CURRENT VS TIME

FOR THREE VOLTAGES

representing the average current vs time following the application of voltage. Similar results are presented in figure 20 for another five current vs time curves. Results given in these two figures are for eight thirty-minute series taken on one sample of isopropyl ether, with an electrode separation of 0.1 cm.

Because of the longer duration of current decay, all measurements taken after those of figure 20 continued for about an hour before removal of voltage.

Figure 21 gives the results obtained on another sample of isopropyl ether. The curves show average current vs time for five series representing three applied voltages with electrode separation constant at 0.1 cm.

Similar series of measurements on another sample of isopropyl ether gave results which are shown in figure 22. The four curves are of four series, at four voltages, and an electrode separation of 0.2 cm. Again average current is plotted against time.

Figure 23 represents four series of measurements of average current vs time. In this case, all four were made with an applied voltage of 225 volts and with an electrode separation of 0.1 cm. These series were made to investigate the progressive changes which occur in the liquid during the course of continued measurements.

Some idea of the dependence of current on applied voltage is given in the curves of figure 24. These curves are of average current (at various times after the application of

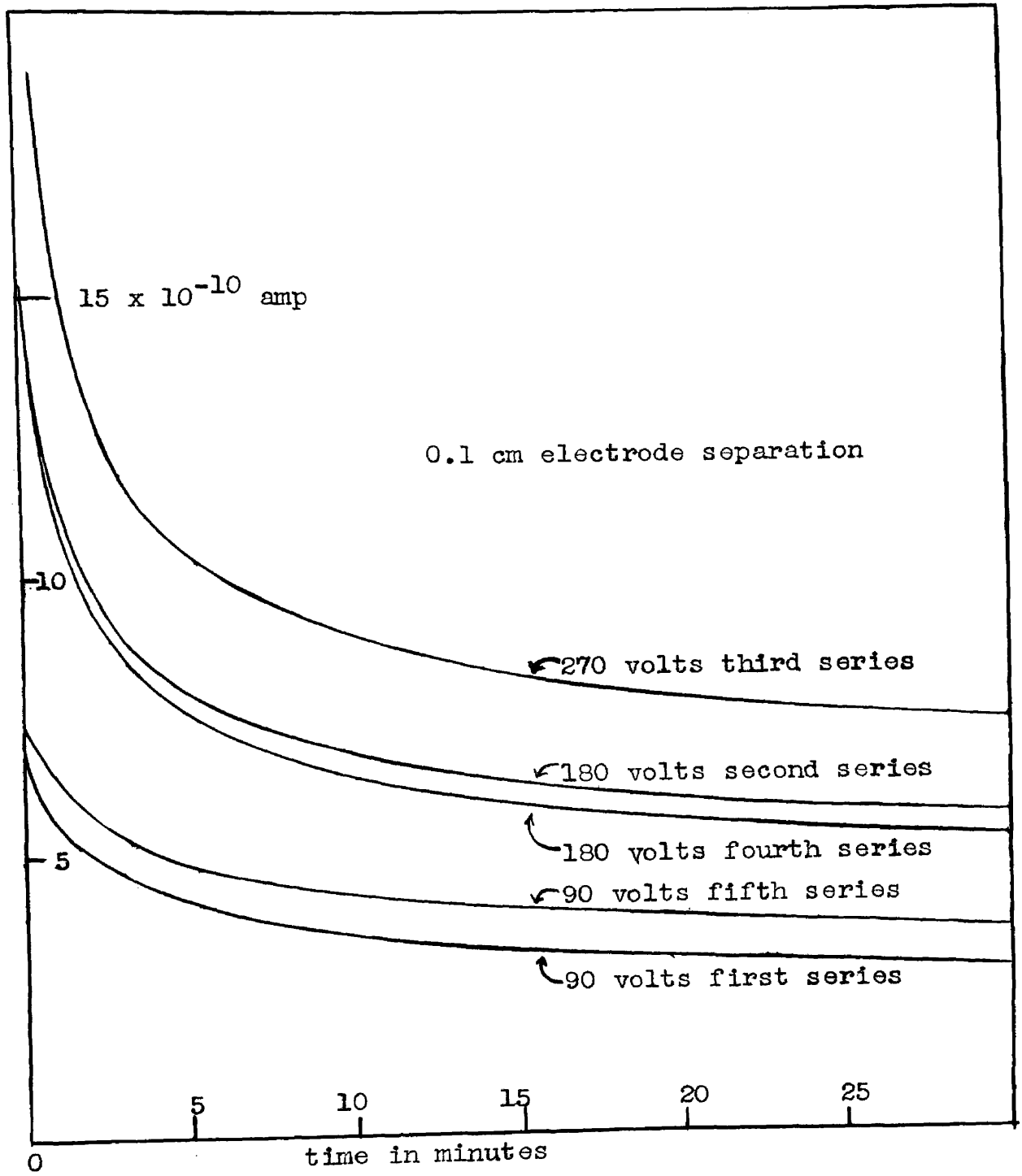


FIGURE XX

ISOPROPYL ETHER

AVERAGE CURRENT VS TIME

FIVE SERIES FOR THREE VOLTAGES

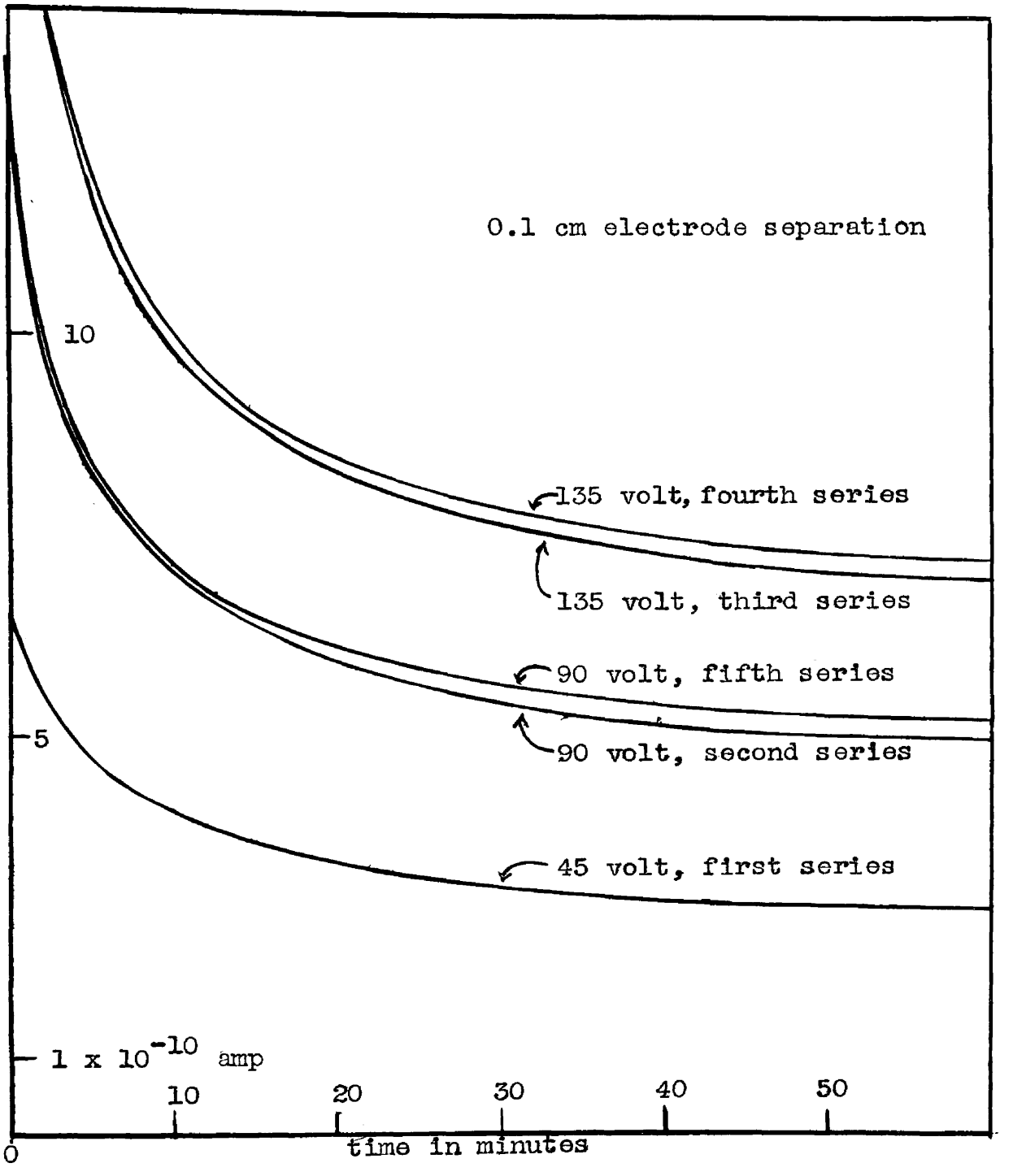


FIGURE XXI

ISOPROPYL ETHER

AVERAGE CURRENT VS TIME

FIVE SERIES FOR THREE VOLTAGES

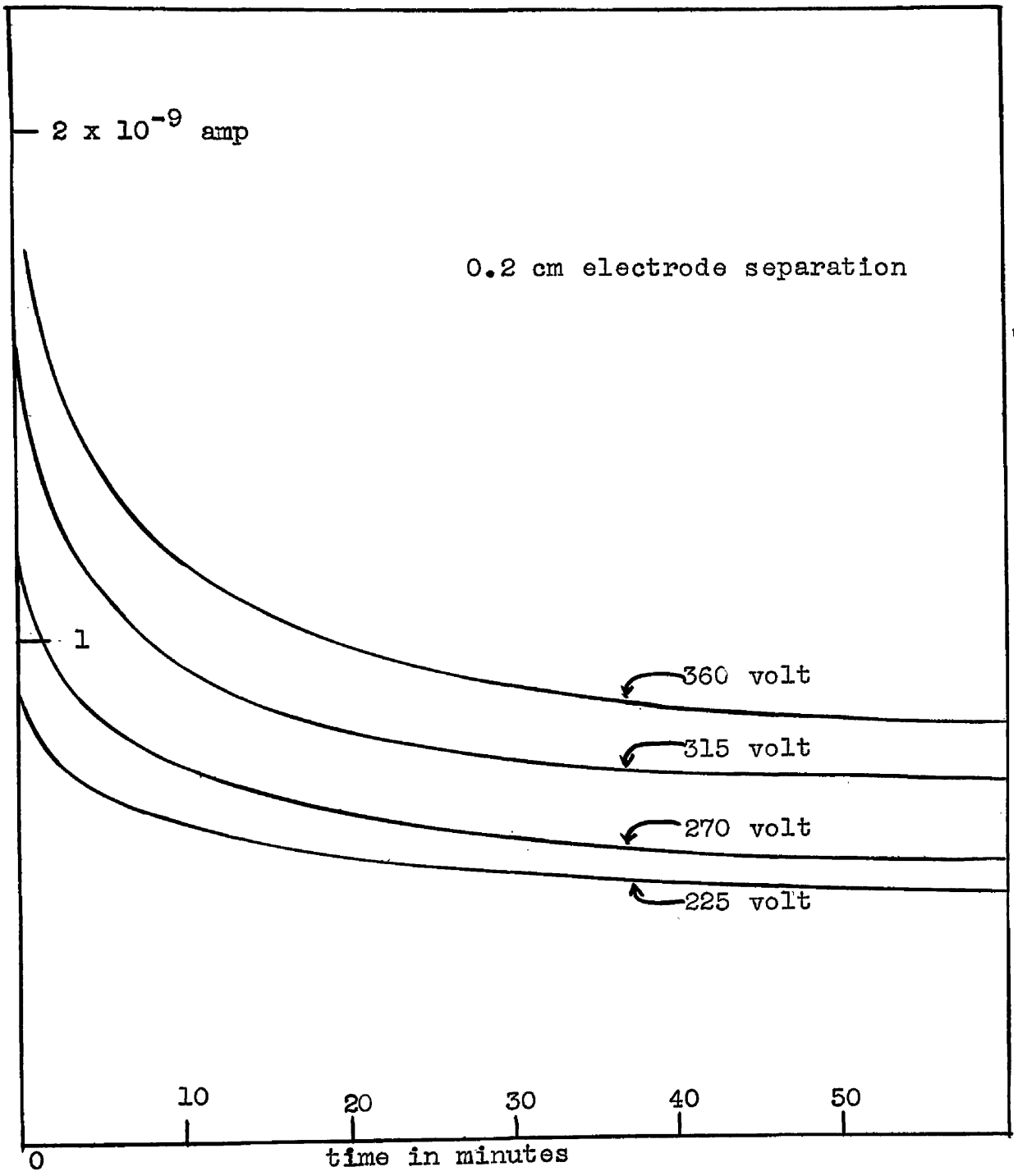


FIGURE XXII

ISOPROPYL ETHER

AVERAGE CURRENT VS TIME

FOUR SERIES FOR FOUR VOLTAGES

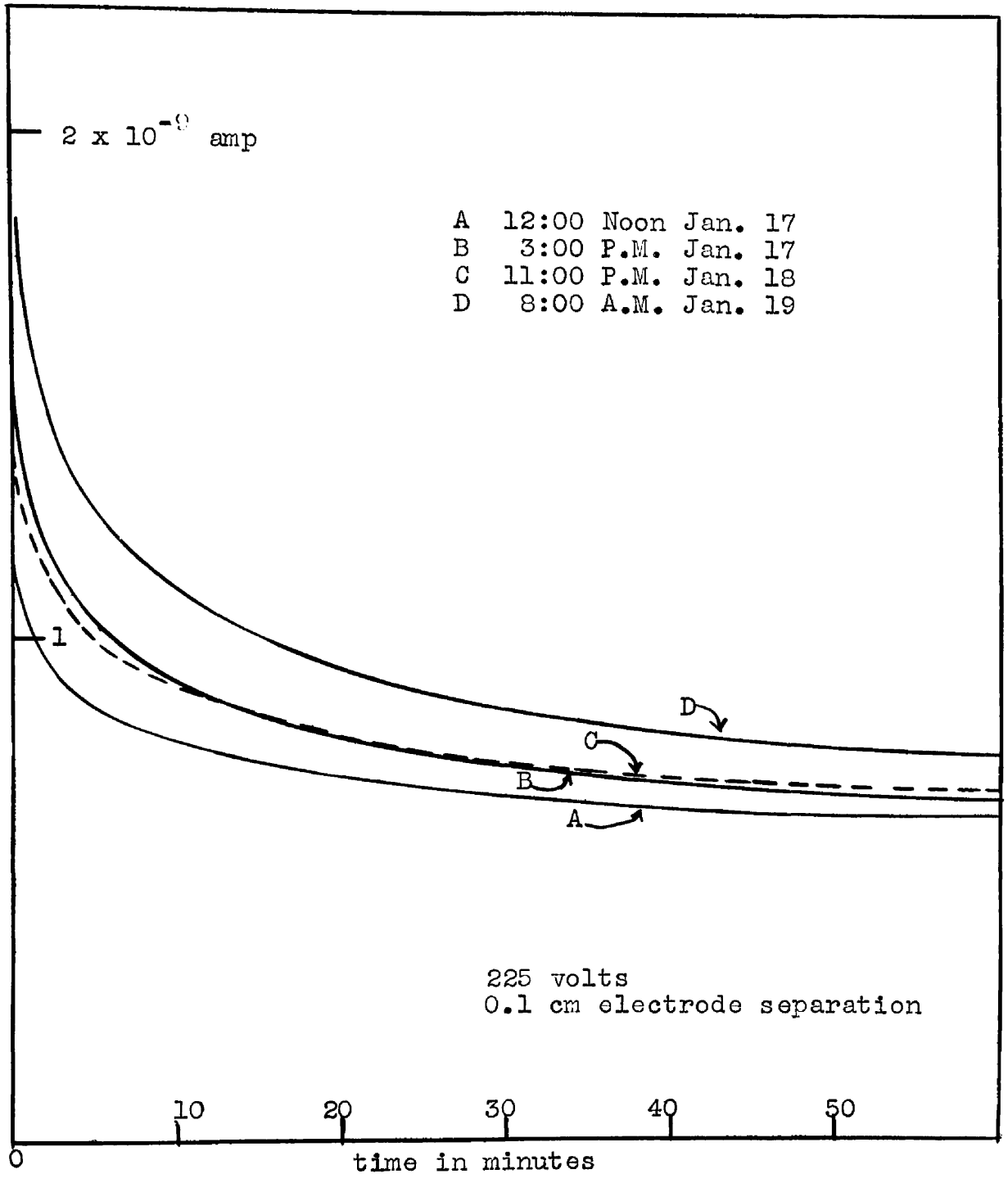


FIGURE XXIII

ISOPROPYL ETHER

AVERAGE CURRENT VS TIME FOR FOUR SERIES

AT THE SAME VOLTAGE AND ELECTRODE SEPARATION

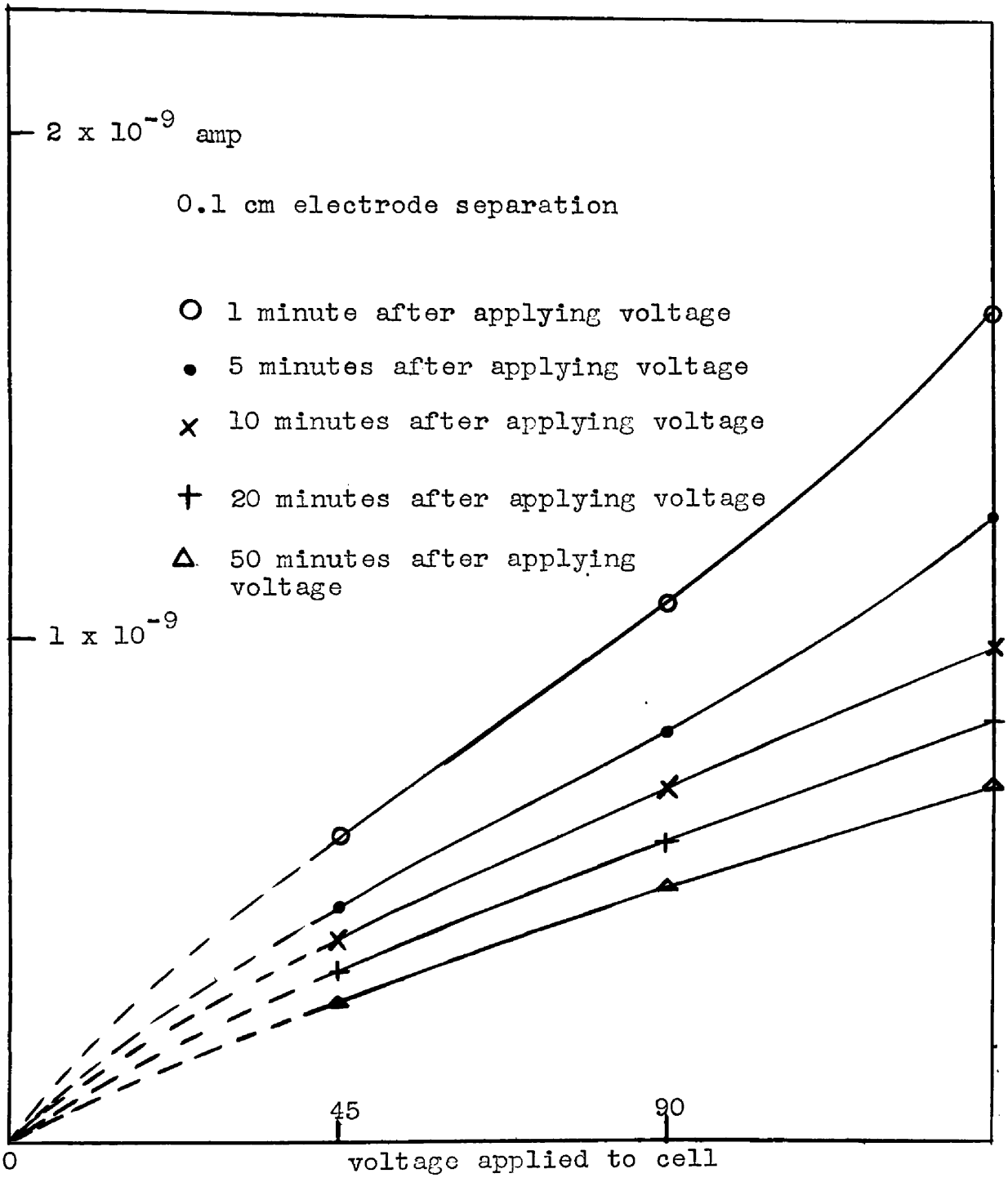


FIGURE XXIV

ISOPROPYL ETHER

CURRENT VS VOLTAGE AT VARIOUS

TIMES AFTER THE APPLICATION OF VOLTAGE

voltage) vs applied voltage.

The analysis and comparison of these results with theory will be given in Chapter V.

3. Bromobenzene With bromobenzene, all satisfactory measurements of current vs time resulted in curves that were very similar to figure 25. The measurements given by this figure were made with 1.5 volts applied across an electrode separation of 0.1 cm.

Qualitative discussion of the bromobenzene results will be given in Chapter V.

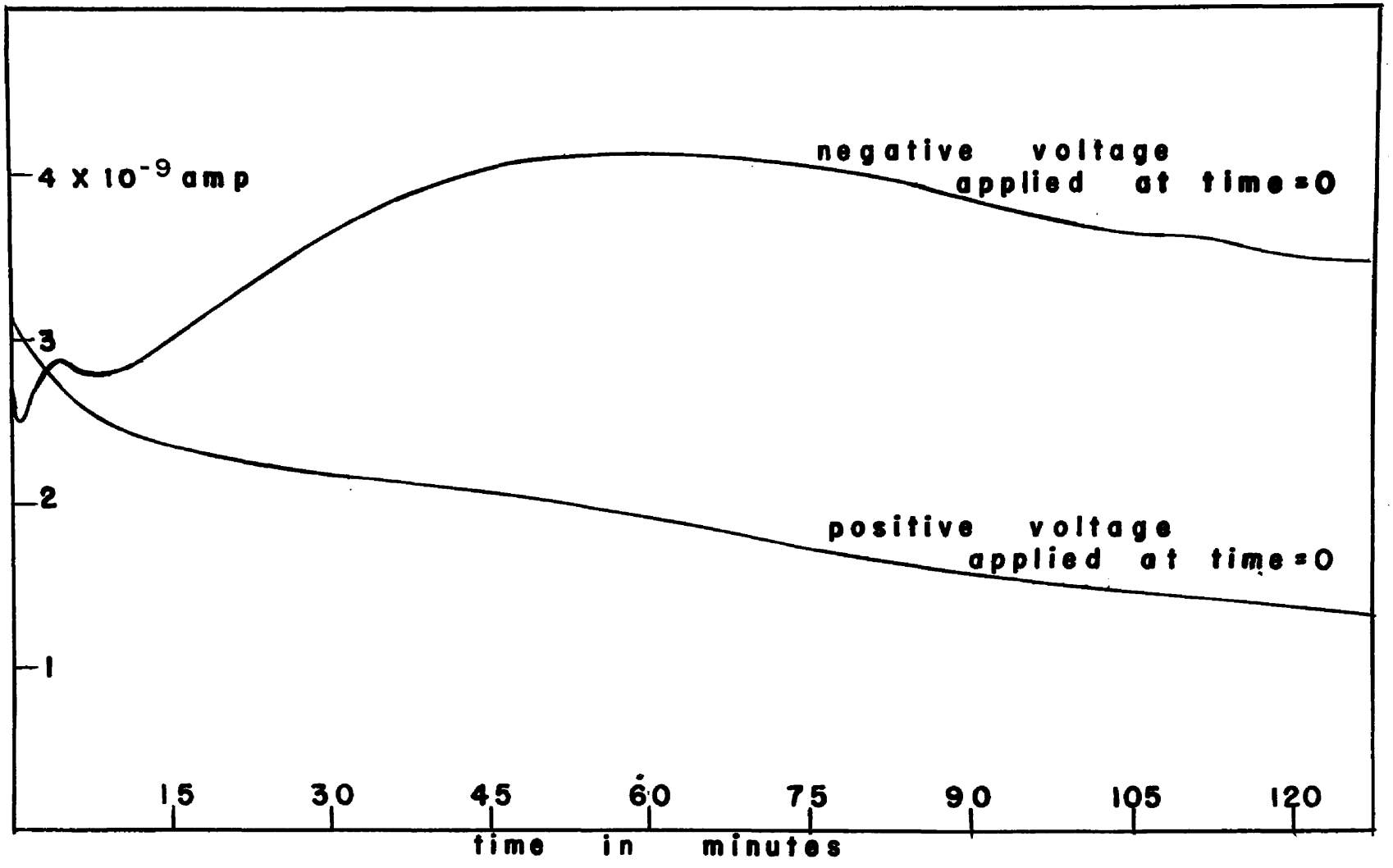


FIGURE XXV

BROMOBENZENE CURRENT VS TIME

CHAPTER IV

THEORY

The theory presented here is that of Dr. George Jaffé. It is essentially that originally developed by him with recent modifications in which he was assisted by Mr. H.C. Chang. The material of this chapter is abstracted from references 15, 16, 17, 18, 19, 20, and 22. The author is particularly indebted to Dr. Jaffé for the use of his theoretical results some of which are pending publication.

A. General Theory

By consideration of all processes which affect the concentration of charge carriers one obtains for one species of carrier pairs

$$\frac{\partial p}{\partial t} = q - \eta n p + D \frac{\partial^2 p}{\partial x^2} - b \frac{\partial (pE)}{\partial x} , \qquad (1)$$

$$\frac{\partial n}{\partial t} = q - \eta n p + D' \frac{\partial^2 n}{\partial x^2} + b' \frac{\partial (nE)}{\partial x} \qquad (2)$$

where x is the distinguished direction. There is also the Poisson equation

$$\frac{\partial E}{\partial x} = \frac{4\pi\epsilon}{K} (p - n). \qquad (3)$$

The symbols in the preceding equations have the following significance:

p = number of positive charge carriers per unit volume,

n = number of negative charge carriers per unit volume,

q = number of carrier pairs produced per unit volume, per unit time,

η = recombination coefficient

D, D' = coefficients of diffusivity for the positive and negative carriers respectively,

b, b' = mobilities of the positive and negative carriers respectively,

E = electric field,

ϵ = elementary charge,

K = dielectric constant.

Thus the time rate of change of concentration of ions of any species is due to production, recombination, diffusion, and migration in the electric field, and the influence of space charge and inhomogeneity of the field.

A first simplification may be made by assuming either that dissociation is complete or that recombination is so rapid that production is at all times in equilibrium with recombination. Either assumption amounts to saying that

$$q - \eta n p = 0 \qquad (4)$$

In its original form the boundary conditions handled two kinds of ions: those of the "first kind" which could transport no charge through the boundary, and those of the "second kind" which were supposed to carry the "stationary"

current. The "ions of the first kind" accounted for the polarization current.

In a more recent formulation of the theory the transport of charge through the boundaries is assumed to be a rate process which is proportional to the difference between the instantaneous carrier concentration and an equilibrium concentration. This assumption is in two parts:

(a) that, in the absence of an applied potential, there exists an equilibrium at the electrodes characterized by definite concentrations p^* and n^*,

(b) and that at the electrodes, $x = 0$ and $x = L$, the rate of discharge is proportional to the differences between the actual concentrations and the equilibrium concentrations.

Thus the boundary conditions become

$$j^+ = -\epsilon\xi(p(0)-p^*),\quad j^- = \epsilon\xi(n(0)-n^*) \text{ at } x=0 \tag{5}$$

and

$$j^+ = \epsilon\xi(p(L)-p^*),\quad j^- = -\epsilon\xi(n(L)-n^*) \text{ at } x=L \tag{6}$$

The quantity ξ is characteristic of the nature of the interface between the electrode and the conduction medium, and it determines the discharge rate. Later in the treatment

it is found to be more convenient to use a dimensionless quantity, ς , to characterize the discharge rate. It is given by

$$\varsigma = \xi \frac{l}{D} \tag{7}$$

where l is the thickness of the polarization layer, that is the distance from the electrode at which polarization effects become negligible. For a first approximation l is assumed to be constant. It is usually much smaller than the electrode separation L.

Subject to the assumptions made so far concerning complete dissociation, equilibrium concentration, and discharge rate; the equations for a single species of ions pairs are

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} - b \frac{\partial (pE)}{\partial x}, \tag{1a}$$

$$\frac{\partial n}{\partial t} = D' \frac{\partial^2 n}{\partial x^2} + b' \frac{\partial (nE)}{\partial x}, \tag{2a}$$

$$\frac{\partial E}{\partial x} = \frac{4\pi\epsilon}{K} (p - n) \tag{3}$$

The current densities, j+ for the positive ions and j- for

the negative ions are given by

$$j^{+} = \epsilon\left(b_p E - D\frac{\partial p}{\partial x}\right), \tag{8}$$

$$j^{-} = \epsilon\left(b' n E - D'\frac{\partial n}{\partial x}\right). \tag{9}$$

Solutions of these are to be obtained subject to the boundary conditions of equations (5) and (6).

This problem is similar to that of heat conduction "with external conduction" and so presents no new mathematical difficulties [38].

The equations (1a), (2a), and (3) are non-linear and can be treated only by successive approximations. However, a formal solution to (1a) and (2a) can be obtained if the field E_1 is assumed to be known. This procedure will then result in an implicit relation for E from equation (3).

The nature of the particular problem to which the theory is applied determines the simplest form that may be assumed for the field. It is not intended that the details of these calculations be included here. It will suffice to give the assumed field, indicate the manner of obtaining a solution, and show the final results for the two applications of theory that are used in this development.

B. A.C. Case

The most general periodic function which may be assumed for the potential V(t) is given by taking the real and

imaginary parts of

$$V(t) = \sum_{m=0}^{\infty} V_m e^{i\omega t} . \tag{10}$$

For small applied voltages of the fundamental frequency, and if higher harmonics may be neglected, a sufficient approximation for V(t) is

$$V(t) = V_0 + V_1 e^{i\omega t} \tag{11}$$

With the small applied voltage, it is reasonable to assume that E, p, n, and j may be expressed by equations of similar form giving:

$$E = E_0 + E_1 e^{i\omega t} , \tag{12}$$

$$p = p_0 + p_1 e^{i\omega t} , \tag{13}$$

$$n = n_0 + n_1 e^{i\omega t} , \tag{14}$$

$$j = j_0 + j_1 e^{i\omega t} . \tag{15}$$

Further, the field must satisfy the relations

$$V_0 = \int_0^l E_0 \, dx , \quad V_1 = \int_0^l E \, dx . \tag{16}$$

Here and in what follows for the ac case, only the two symmetric polarization layers of thickness $l/2$ are considered. This omits the bulk of the liquid, leaving a

total thickness ℓ .

By substitution of equations (11), (12), (13), (14) and (15) into the fundamental equations and considering the boundary conditions an expression for the current density is obtained. With the current density and a suitable choice for the field an expression for the complex admittance can be be obtained. Assuming that in the absence of an applied field the equilibrium concentration extends right up to the electrodes and that there is no dc bias,

$$E_0 = 0, \quad n_0 = p_0 = c_0, \quad j_0 = 0. \tag{17}$$

In addition a sufficiently good approximation for the field is that it is homogeneous,

$$E_1 = \text{Const.} \tag{18}$$

The actual manipulations are quite laborious but are straightforward. It will suffice here to give the results:

$$\frac{1}{R_p} = \frac{1}{R_\infty}\left\{1 - \left[\frac{g_1(\lambda)}{\lambda} + \frac{\rho/2\left(\frac{g_1(\lambda)}{\lambda}\right)^2 + \rho/2\left(\frac{g_2(\lambda)}{\lambda}\right)}{1 + \rho\frac{g_1(\lambda)}{\lambda} + \frac{1}{2}\left(\frac{\rho}{\lambda}\right)^2 g_3(\lambda)}\right]\right\}; \tag{19}$$

$$C_p = \frac{K}{4\pi\ell} + C_0\left\{\frac{\left(\frac{6}{\lambda^3}\right) g_2(\lambda)}{1 + \rho\frac{g_1(\lambda)}{\lambda} + \frac{1}{2}\left(\frac{\rho}{\lambda}\right)^2 g_3(\lambda)}\right\} \tag{20}$$

R_p and C_p are the equivalent parallel resistance and capacitance of the polarization layers. In these equations

$$\lambda = \ell\left(\frac{\omega}{2D}\right)^{\frac{1}{2}} \tag{21}$$

$$s = \xi \frac{l}{D} \tag{7}$$

$$g_1(\lambda) = \frac{\sinh \lambda + \sin \lambda}{\cosh \lambda + \cos \lambda}, \tag{22}$$

$$g_2(\lambda) = \frac{\sinh \lambda - \sin \lambda}{\cosh + \cos \lambda}, \tag{23}$$

$$g_3(\lambda) = \frac{\cosh \lambda - \cos \lambda}{\cosh \lambda + \cos \lambda}, \tag{24}$$

$$\frac{1}{R_\infty} = \frac{2b\epsilon c_0}{l} \tag{25}$$

is the normal conductance reached as $\omega \to \infty$, and

$$C_0 = \frac{\epsilon b c_0 l}{6D} \tag{26}$$

is the maximum capacitance reached as $\omega \to 0$.

C. D.C. Case

In development of solutions for the dc case consideration must be given to the method of observation. As has been stated in Chapter III, this is usually done by measurement of the transient currents produced by the application or removal of a voltage. It is therefore necessary to develop a more general time dependence for the currents following such discontinuities of the applied field. We may, however, use the case for $E = E_0 = \text{const.}$

A general solution to the equations (1a), (2a), and (3) is assumed to be of the form

$$p = p_{stat} + \sum_{m=1}^{\infty} A_m X_m e^{-\lambda_m t}, \tag{27}$$

$$n = n_{stat} + \sum_{m=1}^{\infty} A_m X_m e^{-\lambda_m t}. \tag{28}$$

where p_{stat} and n_{stat} are solutions for $\frac{\partial p}{\partial t} = \frac{\partial n}{\partial t} = 0$, and must be established separately.

In equations (27) and (28) the coefficients A_m and the eigenfunction X_m are established by substitution of (27) and (28) back into (1a), (2a), and (3) and consideration of the initial and boundary conditions.

For the eigenfunctions this yields:

$$X_m = e^{\frac{1}{2}\nu\xi}\left[\cos \nu_m x + \frac{\rho + \nu/2}{Z_m} \sin \nu_m x\right], \tag{29}$$

where the eigenvalues

$$Z_m = \nu_m l \tag{30}$$

are the roots of the trancendental equation

$$\tan Z = \frac{2\rho Z}{\nu^2/4 + Z^2 - \rho^2}. \tag{31}$$

In equations (29) and (31) use has been made of the dimensionless quantities for the voltage

$$v = \frac{b}{D} E_0 l = \frac{b}{D} V, \tag{32}$$

and the discharge constant

$$\rho = \xi \frac{l}{D} \tag{7}$$

The development need only be given for the p-ions since the mathematics for the n-ions is identical.

The coefficients are given by

$$A_m = \frac{\int_0^l \sigma(x)\left[p(x) - p_{stat}\right] X_m \, dx}{\int_0^l \sigma(x) X_m^2 \, dx}, \tag{29}$$

where p(x) is the initial distribution which is assumed to be known and σ (x) is the density factor required to make the differential equation for the eigenfunctions self-adjoint [38]. Its value is given by

$$\sigma(x) = e^{-\frac{\nu x}{l}} \tag{30}$$

It is still necessary to establish the value of p_{stat} which is not an eigenfunction of the x_m, nor can it be included as the term of equation (27) for m = 0. For values of v which are sufficiently large to neglect terms of the order $e^{-\nu}$, the value of p_{stat} is found to be

$$p_{stat} = \frac{p^*\left(\rho + 2\nu e^{-\nu\left(1-\frac{x}{l}\right)}\right)}{\rho + \nu} \tag{31}$$

(1) Charging Current For the case of a charging current following the application of a voltage, the value of p(x) is assumed to be the equilibrium concentration c_o throughout. Results which are sufficiently accurate for practical work are obtained for $\nu \geq 8$. This allows the omission of negligible terms and the simplified expression for the changing current.

$$J = 2\epsilon p^* b E_o \left[\frac{\rho}{\rho + \nu} - 2\left(c_o - p^* \frac{\nu}{\rho+\nu}\right) \sum_{m=1}^{\infty} e^{-\lambda'_m T} C_m \right] \tag{32}$$

is obtained. In equation (32) the dimensionless time variable,

$$T = \left(\frac{D}{l^2}\right) t, \tag{33}$$

and

$$\lambda'_m = \left[\left(\frac{\nu}{2}\right)^2 + Z_m^2\right] \tag{34}$$

are used,

$$C_m = (-1)^m \left[\frac{1}{Z_m^2\left[1 + \left(\frac{\nu}{2Z_m}\right)^2\right]}\right] \frac{D_m}{E_m} \tag{35}$$

with

$$D_m = \left[\left(\frac{\nu}{2}\right)^2 + Z_m^2 + \rho^2\right] - p^2\left[\frac{15}{4}\nu^2 + Z_m^2\right] \tag{36}$$

and

$$E_m = \left[\left(\frac{\nu}{2}\right)^2 + Z_m^2 + \rho^2\right] - \rho^2\nu^2. \tag{37}$$

2. Discharge current In discharge current there is no applied field. Consequently, $E = 0$ is used, as an approximation. Furthermore, equations (27) and (28) are valid with $v = 0$ everywhere but it must be noted that $p_{stat} = p^*$ since the only reasonable concentration to assume for the stationary case is the equilibrium concentration, p^*, as it has been defined earlier.

The general solution for discharge then becomes

$$p^o = p^* + \sum_{m=1}^{\infty} A^o_m X^o_m e^{-\lambda'^o_m T} \tag{38}$$

The superscript zero is used to characterize the discharge case. X^o_m, A^o_m, and λ^o_m are obtained by setting $v = 0$ in the expressions for X_m, A_m, and λ_m.

The evaluation proceeds in much the same manner as for the case of charging currents. It will be sufficient to state the results for contributions due to both positive and negative ions of a single species. For a first approximation

$$J^{o} = -2\epsilon b p^{*} E_{o} \frac{8}{v^{2}} \sum_{m=0}^{\infty} G_{m} e^{-(z^{o}_{2m+1})^{2} T}, \tag{39}$$

$$G_{m} = \left[\left(1 + \left(\frac{z_{2m+1}}{v} \right)^{2} \right) \left(1 + \frac{\rho^{2} + 2\rho}{(z^{o}_{2m+1})^{2}} \right) \right]^{-1}. \tag{40}$$

In order to make the task of analysis more general as well as systematic, theoretical curves were plotted of the normalized current ratio R and R^{o} vs the dimensionless time variable T.

$$R = \frac{J}{2\epsilon b p^{*} E_{o}} = \frac{i}{i_{o}} \tag{41}$$

$$R^{o} = \frac{J^{o}}{2\epsilon b p^{*} E_{o}} = \frac{i^{o}}{i^{o}_{o}}. \tag{42}$$

These curves were calculated for various values of ρ and v, using $p^{*} = c_{o}$. The eigenvalues to use in (41) and (42) were obtained by graphical procedure. Figure 26 shows a family of these curves for the value $v = 8$ and for values of $\rho = 0, 1, 2,$ and 3.

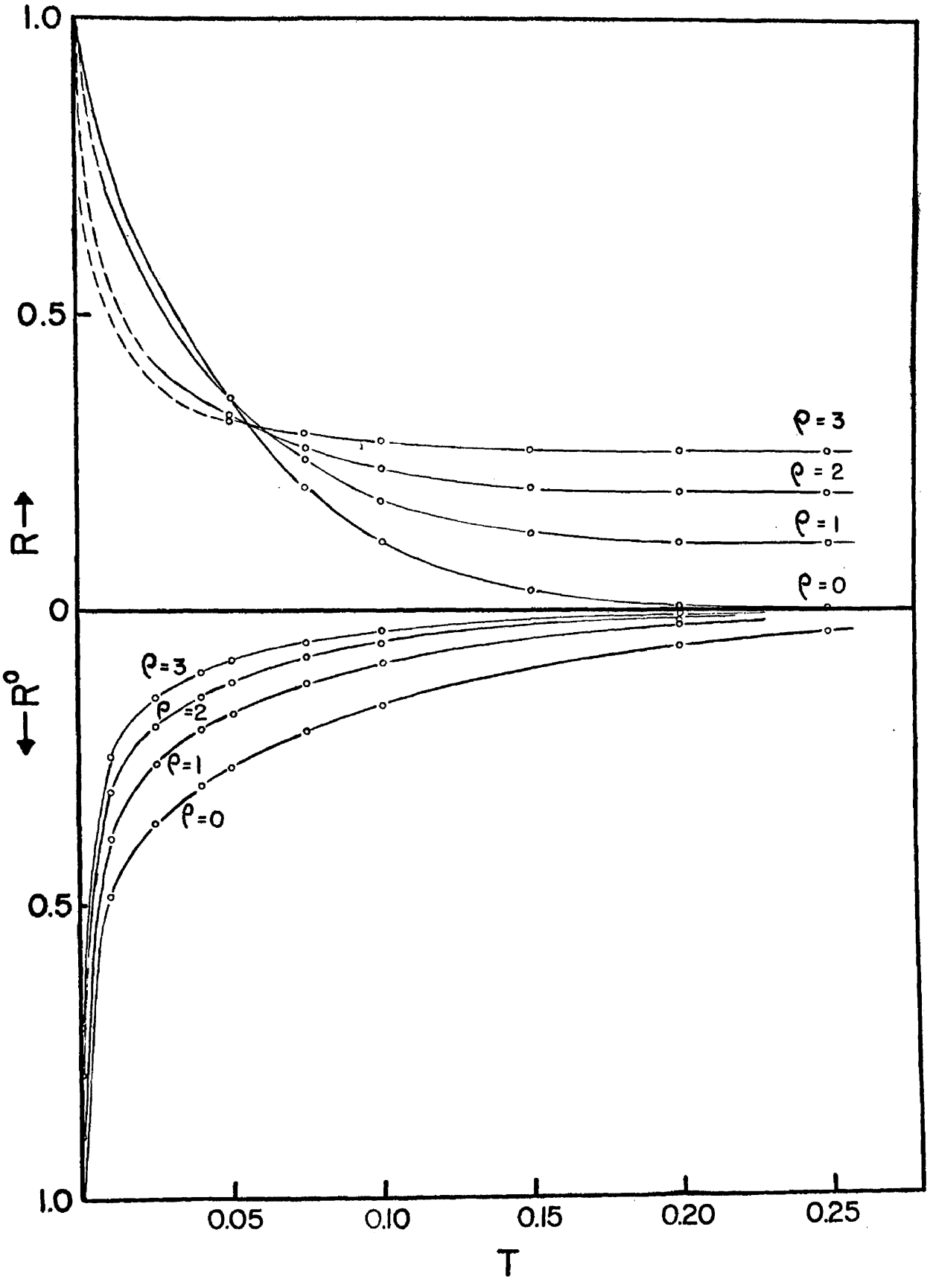


FIGURE XXVII

CURRENT RATIO R VS T

CHAPTER V

ANALYSIS OF RESULTS

In earlier analysis of experimental data on polarization in liquids, the Jaffé theory has been successful in correlating the effects observed in electrolytic solutions and dielectric liquids [19, 20, 22]. In both cases the assumption was made that there existed "slow ions" in addition to the ions of "normal" mobility. With this assumption it was possible to determine physical constants and to fit the theory to the experimental data.

Agreement might have been obtained by including some alternate assumption in the application of the Jaffé theory. For example, recent analysis by Chang indicates that good agreement can be obtained using only one species of ions but assuming the existance of an insulating layer between the electrode and the polarization layer [21b]. Conceivably a combination of slow ions and layer effects is present. It is reported that mobilities in thin films of germanium are found to be much lower than in bulk germanium [39]. Perhaps an insulating layer is formed at the electrode and within this thin film the mobilities are lower than in the liquid bulk or within the polarization layer.

Whatever the nature of the mechanism, it is definite that there is some slow process in addition to the effects of carriers of normal mobility within the bulk and the polarization layers. This will be borne out in the new

material presented on polarization in the intermediate range of conductance.

A. Electrolytic Solutions

Equations (19) and (20) of Chapter IV give the theoretical values of R_p and C_p. These represent the equivalent parallel resistance and capacitance of the polarization layers alone. To compare them with experiment it must be considered that these parallel values are in series with the bulk of the liquid (which has resistance and capacitance) and that the observations are of series resistance and capacitance.

A sketch of the method of analysis will be given by outlining one example. The example chosen is the group of three series represented in figures 5 and 6. These series consist of measurements on water at three electrode separations, using gold-plated electrodes, and covering a frequency range of from 18 cps to 30,000 cps.

The three portions of the resistance curves mentioned in Chapter II may be noted. They are: part (1) - - the low frequency region where the resistance is higher than normal due to polarization, part (2) - - the mid-frequency region which is nearly horizontal and represents the normal "bulk" resistance, and part (3) - - the high frequency end where the resistance drops due to the presence of geometrical capacitance and shunt effects.

In order to reduce the experimental values to the parallel

values of the polarization layers alone, the bulk values have to be subtracted. The normal resistance R'_2, corresponding to the bulk, chosen near the end of part two of the resistance curves, and the bulk geometrical capacitance C'_2, calculated from the area and separation of the plates, had to be augmented by a shunt capacitance representing stray edge effects. A fairly satisfactory fit of the high frequency end of the curves could be realized by choosing for this shunt capacitance a value of $C^* = 100 \mu\mu F$.

After subtraction of the "bulk values" (R'_2 and $1/(C'_2 + C^*)$ from the directly observed values R_s and $1/C_s$, there remain the effective series values of the two polarization layers, namely

$$R'_s = R_s - R'_2, \qquad 1/C'_s = 1/C_s - 1/(C'_2 + C^*) \tag{43}$$

These have to be transformed into the parallel values of conductance $1/R'_p$ and capacitance C'_p in the usual manner. The values obtained in this way should be independent of plate distance, as they refer to the polarization layers alone. This conclusion was verified with good approximation. Finally $1/R'_p$ and C'_p may be compared with the theoretical formulae, equations (19) and (20).

This comparison was done by plotting log $1/R'_p$ and log C'_p versus log $f^{\frac{1}{2}}$ and comparing these curves with families of the theoretical curves of log (R_∞/R_p) log (C_p/C_o). By the vertical and horizontal shifts that are necessary to make the curves coincide, the ionic constants were chosen. It was at this point that it was necessary to introduce the

assumption of "slow ions".

The values of concentrations and mobilities determined for the two species are given in Table V. Having chosen the ionic constants for the two species of ions, it now becomes possible to calculate the actual theoretical curves for comparison with the experimental data. These curves are shown in figures 5 and 6, and the points shown are the experimental observations.

B. D.C. Analysis

For the measurements on hexane and isopropyl ether the analysis was similar. In the direct comparison with the theory, it was found necessary to account for a slow current-decay process. This was done by the assumption of the existance of a species of slow ions, the effect of which could be approximated by a single exponentially decreasing term.

The current was thus assumed to be composed of three parts: the stationary current, i_∞ ; the contribution of the slow ions, $C_2 \exp(-\lambda_1 t)$; and the part due to the fast ions, for which the value is given by the Jaffé theory.

The general method was then to identify and separate these three components, determine the constants graphically, and with these constants, construct the theoretical curve to fit the data.

The first step was to plot $\log(i - i_\infty)/i_\infty$ vs time. This involved a choice of i_∞ . If after some time the

TABLE V

Constants referring to water and used in the calculation of the theoretical curves of figures 5 and 6.

L(cm)	R_2(ohm)	C_2 (F)	C^* (F)
0.1	5240	233	100
0.2	10900	116	100
0.3	15680	77.5	100

$c_1 = 1.37 \times 10^{15}$ cm^{-3} $\quad b_1 = 2.27 \times 10^{-3}$ cm^2/volt sec.

$c_2 = 6.83 \times 10^{15}$ cm^{-3} $\quad b_2 = 2.27 \times 10^{-5}$ cm^2/volt sec.

current decay had been purely exponential, i_∞ could have been determined uniquely. Since this was not the case in these measurements, the choice of i_∞ was to some extent arbitrary. Trial and error indicated that best results were obtained by choosing a value of i_∞ such that, the best straight line was obtained for the portion of the curves between ten minutes and thirty minutes. This straight line portion was then extrapolated back to $t = 0$, and the differences between corresponding points on the straight line and the experimental curve were determined and recorded. These differences represented the portion of the current to be fitted by the summation term of equation (32).

The theoretical values of $\log (i - i_\infty)/i_\infty$ for various values of ρ and t/T were plotted in families of curves such as those shown in figure 27. The logarithms of the differences were then compared with these theoretical curves and the best choice of ρ and the ratio of t/T were obtained.

The coefficients, which were proportional to the concentrations, were determined from the intercept of the extrapolated line representing the slow component and from the vertical shift necessary to fit the theoretical curves to the curve representing the differences.

If there are discharge currents as well as charging currents the experimental values of R and R_o can be plotted to various time scales, and compared to the corresponding theoretical curves of figure 26. A choice can then be made

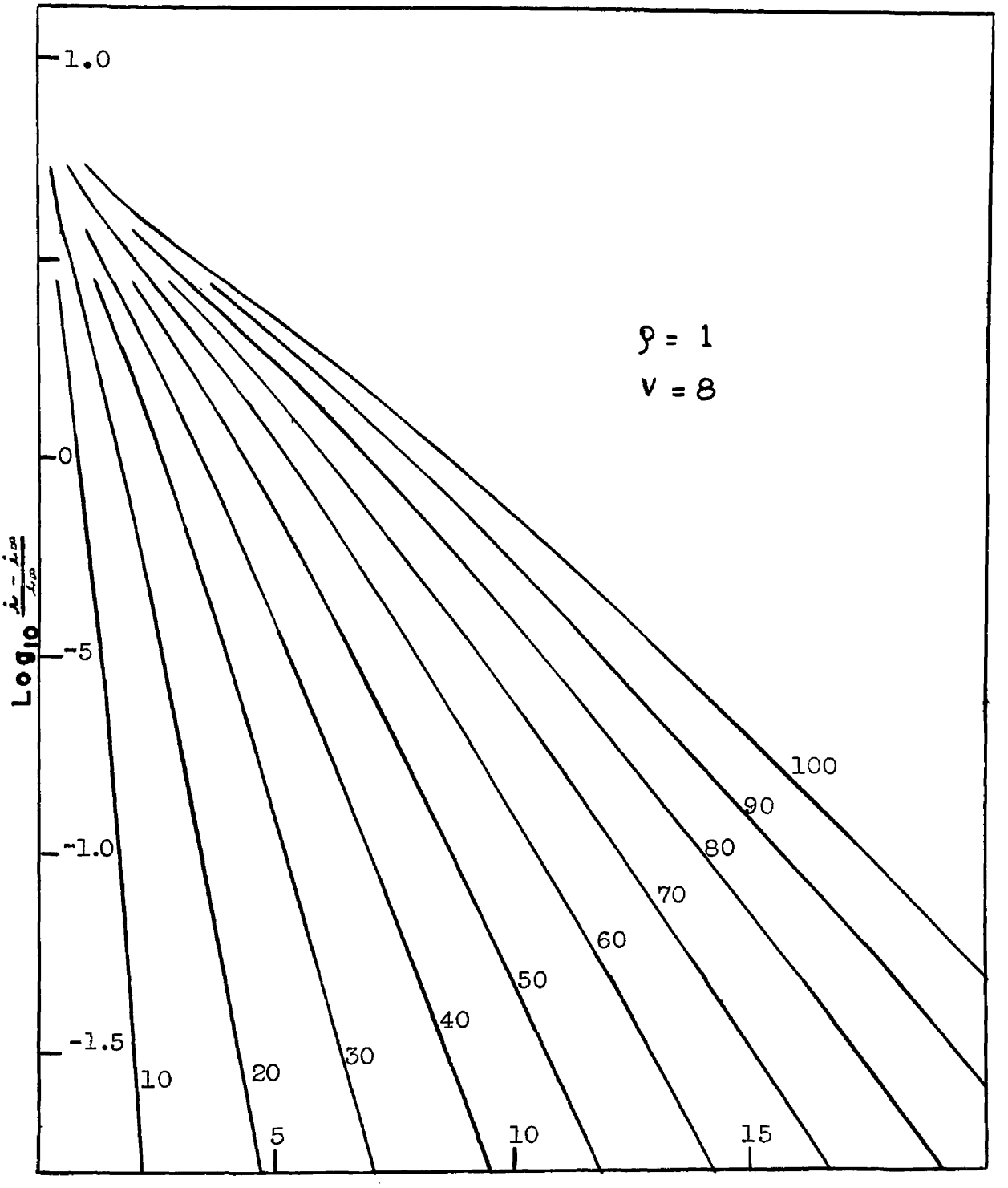


FIGURE XXVII

THEORETICAL CURVES

OF Log $(\frac{i - i_\infty}{i_\infty})$ VS TIME

FOR VARIOUS VALUES OF t/T

for ρ and for the ratio of t/T. This provides a check against the method used with the charging currents alone, since the values for ρ and t/T obtained by the two methods should be the same.

1. Hexane The investigations on hexane were principally directed toward investigation of the effect of electrode separation. The results of the five series given in figure 14 were analyzed and the results are plotted in figure 28. The plotted points are experimental, while the curve is a theoretical one computed from the constants shown on the figure.

All five of these series were taken with different values of electrode separation but with the same field. Considering the uncontrolled changes which occur in the conductance of liquids in this range, it is remarkable that all five series could be fitted this well by a single curve. The deviations from the theoretical curve are not systematic enough to indicate any definite trend.

2. Isopropyl Ether An example of the agreement obtained with isopropyl ether is given in figure 29, which shows the theoretical curve constructed to fit the data given in figure 22. It is apparent from figure 29 that the slow component makes a significant contribution to the conductance of the liquid. The "fast ion" contribution is a small fraction of the total current, and appears to depend on the applied voltage. The theoretical curve could have been made to yield a good fit to any one of the groups of

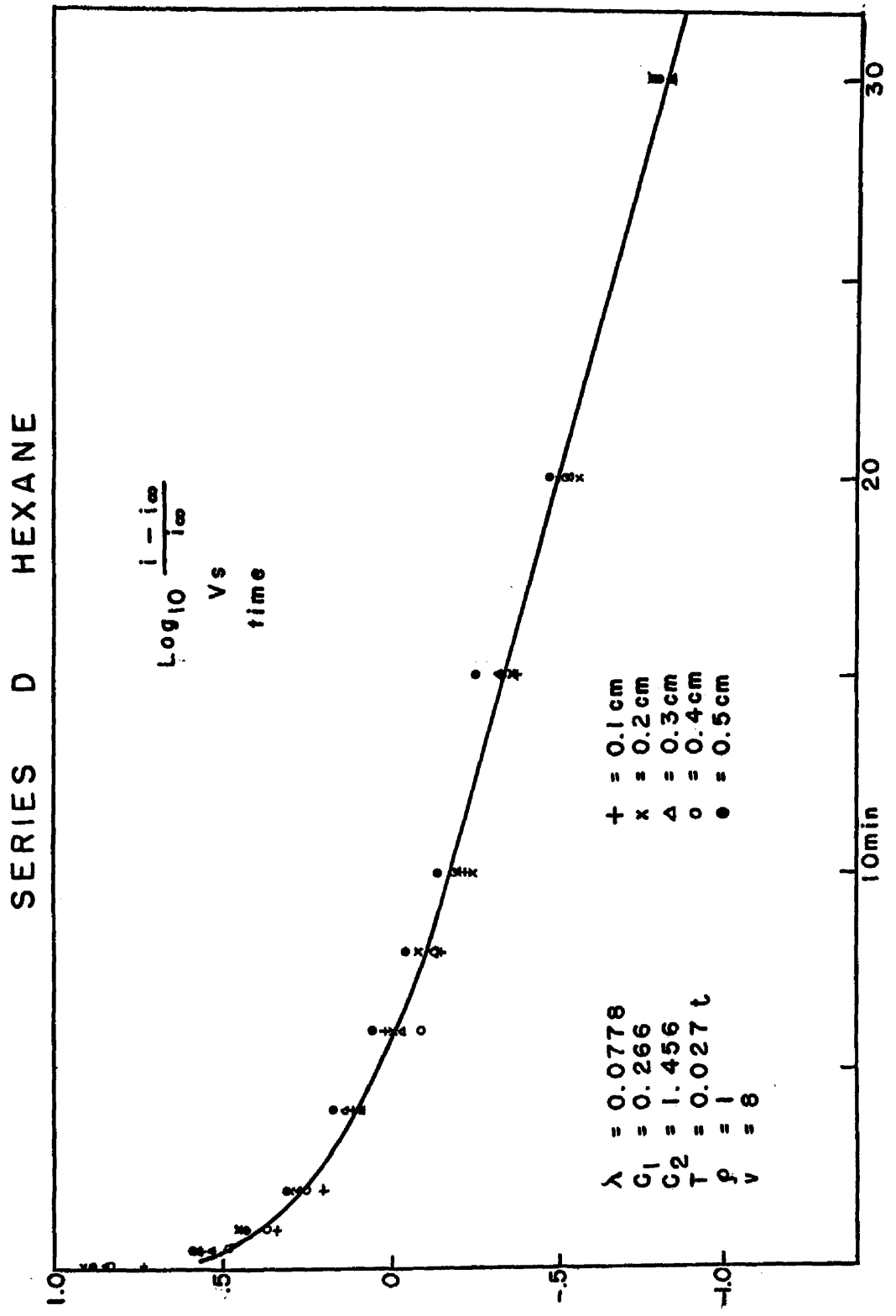


FIGURE XXVIII

HEXANE Log(i - i ∞)/i VS TIME

FOR FIVE ELECTRODE SEPARATIONS

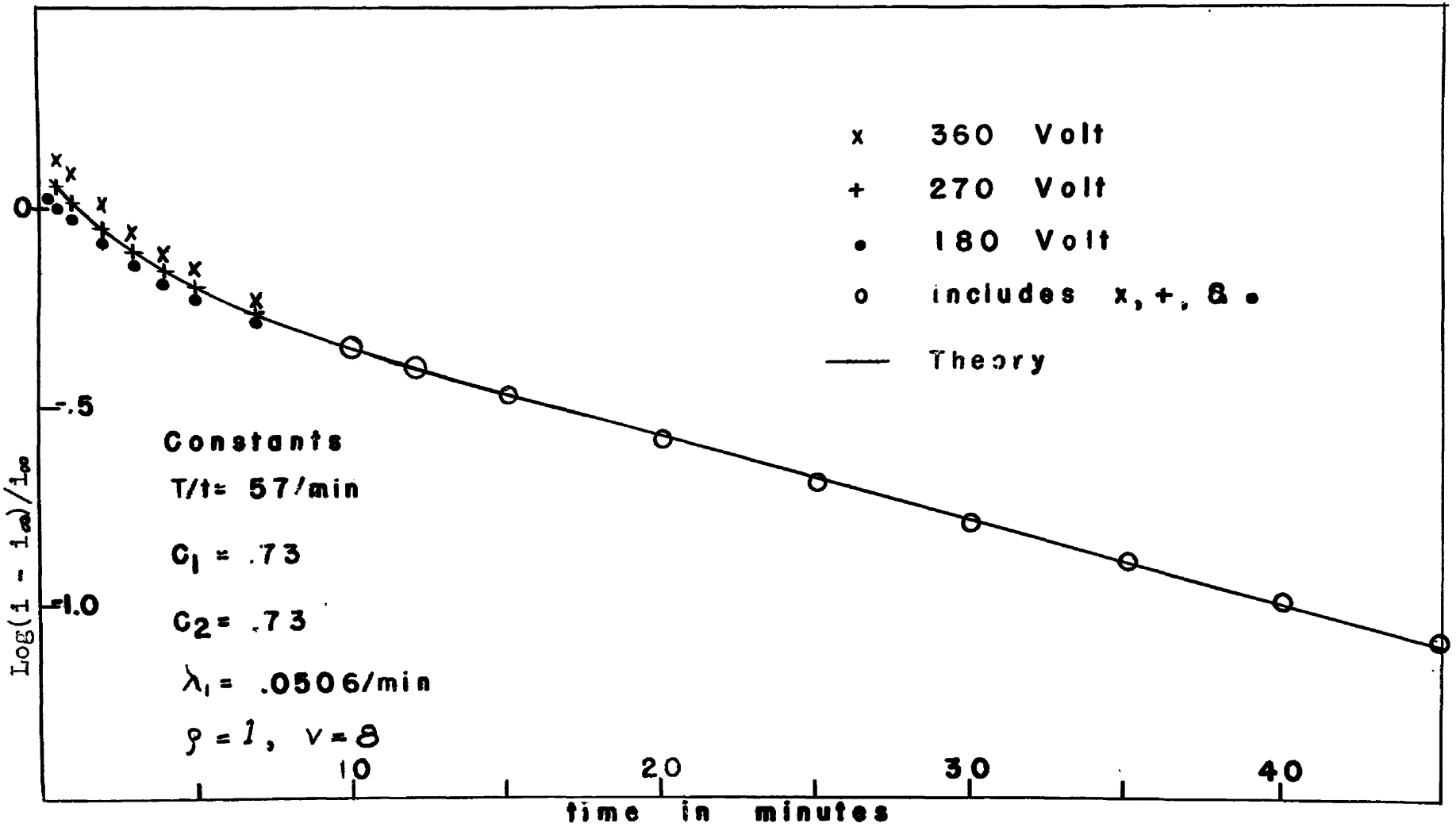


FIGURE XXIX

Log(i - i_∞)/i_∞ VS TIME

ISOPROPYL ETHER

points corresponding to a specific voltage by a slightly different choice of concentration of the fast ions. The constants used in the construction of the theoretical curve are shown on the figure.

3. Bromobenzene No theoretical analysis was performed on the bromobenzene. The effects observed indicate that processes other than polarization and normal conductance were present. It is believed that the asymmetry was the result of asymmetric formation of an extremely thin film on the electrodes. The explanation for formation of such a film may be found in the electrical treatment of the electrodes.

One possible explanation lies in the method of making the observations with the dc amplifier system. In order to observe positive and negative deflections on the recorder scale a small potential (a few hundredths of a volt) was introduced in balancing the amplifier to indicate zero at mid-scale. This potential was always present while the amplifier was being balanced and checked for drift. It is conceivable that the formation of bromide compounds at the surface of the brass electrodes could occur and since there was a slight difference in quiescent potential of the two electrodes an asymmetry could have been introduced.

CHAPTER VI

CONCLUSION

The results of these experiments indicate a general pattern of polarization over all ranges of conductance investigated. The phenomena can be correlated in a uniform way by the Jaffé theory. In every case of conductance through liquids it has been necessary to make an assumption to account for the complete range of time or frequency dependence of the polarization effects. This has been done by the admission of a group of ions of low mobility.

Measurements have been made on electrolytic solutions, water, bromobenzene, isopropyl ether, and hexane. In addition to the general pattern of agreement several specific points are evident.

(1) It was verified experimentally that the polarization effects are independent of electrode separation as long as $L >> \ell$.

(2) In the presence of sufficiently intense ionizing radiation, the dc current reached an equilibrium value almost immediately after the application of a dc voltage and no polarization effects were observable.

(3) In all dc measurements there was asymmetry between the currents observed with opposite polarity of applied voltage. This asymmetry increased with

time after putting a sample into the conductance cell. It also increased during the course of continued measurements, probably due to continued application of voltage.

(4) No discharge currents were observed with isopropyl ether. This absence of discharge current was also noted by Black and Nisbet using certain paraffin oils [40]. They also report the detection (by an induction method) of accumulated space charge in such a case where no discharge occured after the removal of the applied voltage. In the extension of the theory for the dc case to a second approximation Jaffé obtains an additional component of discharge current which represents a migration of charge toward the electrode as a result of the space charge field [22]. This accounts for the reversal of current which LeMay obtained [23]. It might also explain the failure to detect discharge currents in some liquids.

(5) There is indication of the formation of a high resistance electrolytic film on brass electrodes in bromobenzene with the application of voltage.

(6) The dependence of current on voltage is in general not linear for isoproply ether. The slope of the current vs voltage curves depends on the voltage applied and on the time elapsed after the application of the voltage. The dependence

is more nearly linear for observations made a long time after the application of the voltage.

(7) The polarization capacitance is strongly dependent on the electrode material. With KCl the frequency dependence for gold-plated, aluminum, and nickel electrodes was the same although the magnitude differed considerably. However, platinized electrodes showed a completely different frequency dependence.

One of the most interesting possible extensions of this investigation would be toward further measurements on bromobenzene. A few suggestions along this line are given below:

(a) the passage of constant current through a cell containing bromobenzene and the observation of the time dependence of voltage.

(b) measurements with different electrode materials, possibly nickel.

(c) analysis to investigate the possible presence of an insulating film on the electrode surfaces.

(d) use of a measurement system carefully designed to avoid electrical asymmetry for the electrodes.

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VITA

John Allen Rider, Jr. was born in Ponchatoula, Louisiana, July 29, 1920. After attending various public schools in Louisiana, he was graduated from Terrebonne High School in Houma, Louisiana.

He attended Southwestern Louisiana Institute from 1937 to 1940. He was married to Miss Catherine Lorio of New Orleans, May 17, 1940.

He was employed by the U.S. Army Engineers in September 1941. From this time until his entry into the military service he worked on defense construction in the Panama Canal Zone and the Republic of Panama.

In July 1944 he was enlisted in the U.S. Navy and was commissioned in the U.S. Naval Reserve, August 23, 1945.

After being released to inactive duty in May 1946 he reentered Southwestern Louisiana Institute from which he was graduated in June 1948 with the degree of Bachelor of Science in Physics from the College of Education.

In September 1948, he entered Louisiana State University as a graduate student in the department of Physics. After receiving the degree of Master of Science, June 1951, he continued work in the department of Physics in the capacity of research assistant.

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Major Field: Physics

Title of Thesis: Studies of Electrochemical Polarization Liquids of Several Ranges of Conductivity

Approved:

Lloyd W. Morris
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Richard J. Russell
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Date of Examination:

May 9, 1953